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INTERPOLATION OF THE O. S. A. "EXCITATION" DATA BY THE FIFTH-DIFFERENCE OSCULATORY FORMULA[1]

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ABSTRACT

In order to compute the dominant wave length and purity of a color stimulus by means of the O. S. A. "excitation" data, two values must be obtained by interpolation. The adoption of the osculatory formula for this interpolation permits the computations to be made with perfect reproducibility. Each of the O. S. A. curves by this method is represented as a series of parabolas of the fifth degree which join at the values specified at every 10 mμ so as to have a common slope and curvature at the junction point. Interpolated values have been computed according to this formula for every millimicron.

Since 1922, colorimetric computation in America has been carried out mostly by means of the O. S. A. "excitation" data[2] in their extrapolated form.[3] In spite of the fact that these data are based on rather meager experimental measurements they represent the characteristics of the average, normal eye with a satisfactory degree of approximation, and they have been used as the basis for extensive work in color standardization. In computing dominant wave length and colorimetric

[1] Publication Approved by the Director of the Bureau of Standards of the U. S. Department of Commerce.

[2] L. T. Troland, *Report of the Committee on Colorimetry for 1920–21*, J.O.S.A. and R.S.I., *6*, 547–553; 1922.

[3] *Spectrophotometry; Report of O. S. A. Progress Committee for 1922–3*, J.O.S.A. and R.S.I., *10*, 230; 1925.

purity[4] by means of these data interpolated values are required and have commonly been found from an interpolation graph.

It is not to be supposed, of course, that any form of interpolation, graphical or by formula, yields any information concerning the true course of the O. S. A. "excitation" curves between the specified points. Theoretically that course is wholly unspecified, and there are a large number of equally reliable curves to be drawn through the intervals. As in the case of the standard visibility function[5] it has been found convenient in the work of the National Bureau of Standards to adopt arbitrarily a single set of curves. The interpolated values adopted are found by a method superior to any graphical interpolation because the values may be reproduced at any time anywhere, and it is believed that the solution by fifth-difference, osculatory interpolation is more suitable than solutions by other formulas for interpolation because it combines continuity in function, in first derivative and in second derivative with considerable computational convenience. Indeed, the ease of applying this method is so great that the labor involved is not much greater than that of the graphical method.

If λ be the wave length in millimicrons, λ_0, the value of the wave length at the beginning of the 10 mμ interval within which $f(\lambda-\lambda_0)$ is to be defined by interpolation, and if $\Delta_1 f(-20), \cdots, \Delta_5 f(-20)$ be the five leading major differences, then the fifth-difference, osculatory-interpolation formula may be written:

$$f(\lambda-\lambda_0) = f(-20) + k_1\Delta_1 f(-20) + k_2\Delta_2 f(-20) + k_3\Delta_3 f(-20) + k_4\Delta_4 f(-20) + k_5\Delta_5 f(-20), \quad \lambda_0 < \lambda < \lambda_0 + 10$$

where the coefficients, k_1 to k_5, applied to the leading major differences are defined:

$$k_1 \equiv (\lambda-\lambda_0+20)/10$$

$$k_2 \equiv (\lambda-\lambda_0+20)(\lambda-\lambda_0+10)/200$$

$$k_3 \equiv (\lambda-\lambda_0+20)(\lambda-\lambda_0+10)(\lambda-\lambda_0)/6{,}000$$

$$k_4 \equiv (\lambda-\lambda_0+20)(\lambda-\lambda_0+10)(\lambda-\lambda_0)(\lambda-\lambda_0-10)/240{,}000$$

$$k_5 \equiv (\lambda-\lambda_0)^3(\lambda-\lambda_0-10)(5\lambda-5\lambda_0-70)/2{,}400{,}000$$

[4] I. G. Priest, *The Computation of Colorimetric Purity*, J.O.S.A. and R.S.I., *9*, 503–520; 1924. D. B. Judd, *The Computation of Colorimetric Purity*, J.O.S.A. and R.S.I., *13*, 133–152; 1926.

[5] D. B. Judd, *Extension of the Standard Visibility Function to Intervals of 1 Millimicron by Third-difference Osculatory Interpolation*, B. S. Jour. Research, *6*, 465–471; 1931; J.O.S.A., *21*, 267–275; 1931.

This formula is another form of that derived in 1880 by Sprague.[6] Sprague's formula was restated in nearly the form used above by Karup[7] twenty years later who used, however, three of the central differences in place of three of the leading differences which we have used here with appropriate changes in the coefficients of these differences. Since this formula, applied interval by interval, yields a series of parabolas which join at the specified points so as to have common slopes and osculating circles at the junction points, it was called by Karup a formula for osculatory interpolation. Osculatory interpolation has attracted some attention[8] since its discovery, and, indeed, has been extensively used in the construction of the United States Life Tables.[9] Probably the best general treatment of osculatory interpolation is due to Glover.[10]

Although the formulas for osculatory interpolation have usually been applied in the past by computing the leading minor differences (that is, values which would be obtained by differencing the desired, evenly spaced, interpolated values) from the leading major differences, and then deriving the desired interpolated values by continuous addition, the interpolation of the O. S. A. "excitation" data has been accomplished by finding for each value the products indicated in the formula and actually taking their sum. With a computing machine it was found possible to obtain nine interpolated values and to check them by an independent method in about twenty minutes;[11] it seems doubtful whether the continuous addition method would be much more expeditious.

[6] T. B. Sprague, *Explanation of a New Formula for Interpolation*, J. Inst. Actuaries, *22*, 270–285; 1880.

[7] J. Karup, *On a New Mechanical Method of Graduation*, Trans. Second International Actuarial Congress, 82; 1899.

[8] George King, *On the Construction of Mortality Tables from Census Returns and Records of Deaths*, J. Inst. Actuaries, *42*, 238–246; 1908. James Buchanan, *Osculatory Interpolation by Central Differences; with an Application to Life Table Construction*, J. Inst. Actuaries, *42*, 369–394; 1908; see also an appendix by G. J. Lidstone, Alternative Demonstration of the Formula for Osculatory Interpolation, pp. 394–397. George King, *On a New Method of Constructing and of Graduating Mortality and Other Tables*, J. Inst. Actuaries, *43*, 109–184; 1909.

[9] J. W. Glover, *United States Life Tables*, 1890, 1901, 1910, and 1901–1910, 344–347, 372–388; 1921.

[10] J. W. Glover, *Derivation of the United States Mortality Table by Osculatory Interpolation*, Quarterly Publications of the American Statistical Association, *12*, 87–93; 1910.

[11] The check was carried out by taking the differences in the ascending order rather than in the descending order as indicated in the formula. See Tables 2 and 4. It might naturally be supposed that about twice the time to calculate nine values would be required to calculate and check them by an independent method, but this is not quite the case. The time actually required is considerably less than twice because the products found for checking the values in one interval may be used to calculate values in the four subsequent intervals.

We take, then, $\lambda-\lambda_0$ equal in succession to 1, 2, $\cdots$ 9, and $f(\lambda-\lambda_0)$ interval by interval equal to ρ_0, γ_0 and β_0 in succession, where ρ_0, γ_0 and β_0 are the O. S. A. "excitation curves" as extrapolated by Priest and Gibson.[12]

Table 1 shows by an example how to compute the leading, descending, major differences; we have taken $f(\lambda-\lambda_0)$ equal to ρ_0, and λ_0 equal to 580 mμ. The leading, descending, major differences appear in the first row.

TABLE 1. *Computation of the leading descending major differences, $\lambda_0=580$ mμ.*

$\lambda-\lambda_0$ in mμ	λ in mμ	$f(\lambda-\lambda_0)$ $=\rho_0$	$\Delta_1\rho_0$	$\Delta_2\rho_0$	$\Delta_3\rho_0$	$\Delta_4\rho_0$	$\Delta_5\rho_0$
−20	560	466	+39	−24	+24	−64	+121
−10	570	505	+15	0	−40	+57	
0	580	520	+15	−40	−17		
10	590	535	−25	−23			
20	600	510	−48				
30	610	462					

Table 2 shows by the same example the computation of the leading, ascending, major differences which were used in an independent check on the computation; the leading, ascending, major differences appear in the first row of this table.

TABLE 2. *Computation of the leading ascending major differences, $\lambda_0=580$ mμ.*

$\lambda-\lambda_0$ in mμ	λ in mμ	$f(\lambda-\lambda_0)$ $=\rho_0$	$\nabla_1\rho_0$	$\nabla_2\rho_0$	$\nabla_3\rho_0$	$\nabla_4\rho_0$	$\nabla_5\rho_0$
30	610	462	+48	−23	−17	+57	−121
20	600	510	+25	−40	+40	−64	
10	590	535	−15	0	−24		
0	580	520	−15	−24			
−10	570	505	−39				
−20	560	466					

Table 3 gives the values of the coefficients, k_1 to k_5, for $\lambda-\lambda_0$ equal to 1, 2, $\cdots$ 9.

Table 4 shows the details of the computation of the interpolated values according to the fifth-difference formula for the same interval and

[12] See footnote 3, p. 531. The values referred to here are included in Table 5 along with the values obtained from them by interpolation.

TABLE 3. *Coefficients, k_1 to k_5, for interpolation to tenths by fifth-difference osculatory interpolation.*

$\lambda-\lambda_0$	k_1	k_2	k_3	k_4	k_5
1	+2.1	+1.155	+0.0385	−0.0086625	+0.00024375
2	+2.2	+1.320	+ .0880	− .0176000	+ .00160000
3	+2.3	+1.495	+ .1495	− .0261625	+ .00433125
4	+2.4	+1.680	+ .2240	− .0336000	+ .00800000
5	+2.5	+1.875	+ .3125	− .0390625	+ .01171875
6	+2.6	+2.080	+ .4160	− .0416000	+ .01440000
7	+2.7	+2.295	+ .5355	− .0401625	+ .01500625
8	+2.8	+2.520	+ .6720	− .0336000	+ .01280000
9	+2.9	+2.755	+ .8265	− .0206625	+ .00759375

TABLE 4. *Example of interpolation to tenths by the fifth-difference osculatory formula, descending differences; check by ascending differences.*

Take $\lambda_0=580$ mμ, and $f(\lambda-\lambda_0)=\rho_0$; then from Table 1:

$$f(\lambda-\lambda_0)=466+39\,k_1-24\,k_2+24\,k_3-64\,k_4+121\,k_5.$$

The coefficients, k_1 to k_5, may be found in Table 3.

λ in mμ	$\lambda-\lambda_0$	$+39\,k_1$	$-24\,k_2$	$+24\,k_3$	$-64\,k_4$	$+121\,k_5$	$f(\lambda-\lambda_0)$
581	1	+ 81.90	−27.72	+ 0.92	+0.56	+0.02	521.68
582	2	+ 85.80	−31.68	+ 2.11	+1.13	+ .19	523.55
583	3	+ 89.70	−35.88	+ 3.59	+1.68	+ .52	525.61
584	4	+ 93.60	−40.32	+ 5.38	+2.15	+ .97	527.78
585	5	+ 97.50	−45.00	+ 7.50	+2.50	+1.42	529.92
586	6	+101.40	−49.92	+ 9.98	+2.66	+1.74	531.86
587	7	+105.30	−55.08	+12.85	+2.57	+1.82	533.46
588	8	+109.20	−60.48	+16.13	+2.15	+1.55	534.55
589	9	+113.10	−66.12	+19.84	+1.32	+ .92	535.06

Check by ascending differences; from Table 2 we may write:

$$f(\lambda-\lambda_0)=462+48\,k_1'-23\,k_2'-17\,k_3'+57\,k_4'-121\,k_5'$$

The coefficients, k_1' to k_5', may be found in Table 3 by reading the values of the coefficients, k_1 to k_5, for $10-\lambda+\lambda_0$ instead of for $\lambda-\lambda_0$.

λ in mμ	$\lambda-\lambda_0$	$+48\,k_1'$	$-23\,k_2'$	$-17\,k_3'$	$+57\,k_4'$	$-121\,k_5'$	$f(\lambda-\lambda_0)$
581	1	+139.20	−63.36	−14.05	−1.18	−0.92	521.69
582	2	+134.40	−57.96	−11.42	−1.92	−1.55	523.55
583	3	+129.60	−52.79	− 9.10	−2.29	−1.82	525.60
584	4	+124.80	−47.84	− 7.07	−2.37	−1.74	527.78
585	5	+120.00	−43.13	− 5.31	−2.23	−1.42	529.91
586	6	+115.20	−38.64	− 3.81	−1.92	− .97	531.86
587	7	+110.40	−34.39	− 2.54	−1.49	− .52	533.46
588	8	+105.60	−30.36	− 1.50	−1.00	− .19	534.55
589	9	+100.80	−25.56	− .65	− .50	− .02	535.07

function referred to in Tables 1 and 2. The check by means of the ascending differences is also given for this interval and function.

Table 5 gives the results of these computations for ρ_0, γ_0 and β_0.[13] Since there was some rejection error in writing down the products (for example, the coefficients, k_1 to k_5, given in Table 3 were taken to the nearest fourth decimal), the values given in Table 5 are not quite what would be found by rigorous evaluation according to the formula for fifth-difference osculatory interpolation; they may be taken as correct, however, to within 3 in the second decimal. The values of Table 5 were further checked for clerical errors by computing the first and second minor differences.

TABLE 5. *The O.S.A. "Excitation" Curves extended to values for every millimicron by fifth-difference osculatory interpolation.*

λ in mμ	ρ_0	γ_0	β_0	λ in mμ	ρ_0	γ_0	β_0
410	0	0	433	430	0	3	915
1	0.00	0.05	450.34	1	0.00	3.28	936.48
2	0.00	0.11	466.85	2	0.00	3.58	955.33
3	0.00	0.19	482.53	3	0.00	3.91	971.38
4	0.00	0.27	497.65	4	0.00	4.26	984.68
5	0.00	0.37	512.88	5	0.00	4.64	995.42
6	0.00	0.49	528.98	6	0.00	5.06	1003.81
7	0.00	0.61	546.72	7	0.00	5.50	1010.18
8	0.00	0.73	566.71	8	0.00	5.96	1014.76
9	0.00	0.86	589.18	9	0.00	6.47	1017.68
420	0	1	614	440	0	7	1019
1	0.00	1.15	640.68	1	0.00	7.59	1018.48
2	0.00	1.30	669.70	2	0.00	8.21	1015.95
3	0.00	1.47	701.04	3	0.00	8.89	1011.45
4	0.00	1.66	734.21	4	0.00	9.62	1005.18
5	0.00	1.85	768.20	5	0.00	10.44	997.49
6	0.00	2.05	801.90	6	0.00	11.33	988.76
7	0.00	2.28	834.20	7	0.00	12.32	979.38
8	0.00	2.50	864.09	8	0.00	13.43	969.69
9	0.00	2.74	891.04	9	0.00	14.65	959.88

[13] The values for ρ_0 from 451 to 459 and from 461 to 469 mμ result from substituting in the formula $f(-20)$ equal to 4 and 1, respectively; that is, we have taken ρ_0 for 430 and 440 mμ equal to ρ_0 for 470 and 460 mμ, respectively, instead of zero as shown in Table 5. This choice was made in order to bring the interpolated function to zero at 450 mμ with a zero slope; then, for λ less than 450 mμ, ρ_0 is arbitrarily set at zero instead of at the values which would be obtained by mechanical application of the formula. Similarly for β_0 between 590 and 610 mμ, we choose β_0 in the formula as 1 and 2 for 620 and 630, respectively, although β_0 is given in Table 5 as zero for wave lengths greater than 610 mμ.

TABLE 5. (*Continued*)

λ in mμ	ρ_0	γ_0	β_0	λ in mμ	ρ_0	γ_0	β_0
450	0	16	950	490	41	169	220
1	0.01	17.48	939.91	1	44.44	175.86	202.72
2	0.05	19.06	929.69	2	47.97	183.19	187.64
3	0.11	20.74	919.44	3	51.62	191.02	174.83
4	0.20	22.54	909.12	4	55.39	199.36	164.12
5	0.31	24.52	898.68	5	59.32	208.20	155.18
6	0.43	26.68	888.06	6	63.47	217.55	147.56
7	0.56	29.10	877.15	7	67.88	227.42	140.83
8	0.70	31.78	865.86	8	72.60	237.79	134.60
9	0.85	34.76	854.14	9	77.64	248.66	128.66
460	1	38	842	500	83	260	123
1	1.17	41.51	829.55	1	88.64	271.80	117.84
2	1.35	45.31	816.89	2	94.59	284.06	113.19
3	1.56	49.42	804.02	3	100.82	296.78	108.98
4	1.79	53.77	790.90	4	107.34	309.88	105.16
5	2.06	58.32	777.31	5	114.12	323.27	101.64
6	2.35	62.95	763.10	6	121.13	336.84	98.40
7	2.69	67.60	748.08	7	128.33	350.49	95.36
8	3.07	72.17	732.08	8	135.74	364.11	92.46
9	3.51	76.64	715.05	9	143.30	377.62	89.69
470	4	81	697	510	151	391	87
1	4.55	85.30	678.06	1	158.86	404.25	84.36
2	5.16	89.54	658.31	2	166.89	417.40	81.69
3	5.83	93.74	637.78	3	175.08	430.43	78.97
4	6.57	97.88	616.48	4	183.38	443.22	76.20
5	7.41	101.97	594.40	5	191.76	455.73	73.42
6	8.39	106.01	571.56	6	200.16	467.80	70.70
7	9.50	110.01	547.94	7	208.52	479.33	68.06
8	10.81	114.01	523.60	8	216.80	490.24	65.55
9	12.31	118.00	498.58	9	224.96	500.47	63.20
480	14	122	473	520	233	510	61
1	15.88	126.02	446.93	1	240.92	518.87	58.89
2	17.97	130.02	420.08	2	248.70	527.01	56.87
3	20.28	134.01	392.56	3	256.34	534.39	54.92
4	22.80	138.04	364.62	4	263.82	541.08	53.06
5	25.50	142.24	336.87	5	271.18	547.13	51.26
6	28.38	146.68	309.88	6	278.44	552.70	49.52
7	31.38	151.50	284.32	7	285.63	557.89	47.84
8	34.48	156.81	260.67	8	292.78	562.80	46.19
9	37.69	162.64	239.24	9	299.92	567.51	44.58

TABLE 5. (*Continued*)

λ in mμ	ρ_0	γ_0	β_0	λ in mμ	ρ_0	γ_0	β_0
530	307	572	43	570	505	517	7
1	314.02	576.22	41.46	1	507.51	508.54	6.67
2	320.98	580.13	39.96	2	509.64	499.62	6.34
3	327.91	583.77	38.48	3	511.33	490.24	6.02
4	334.76	587.14	37.03	4	512.68	480.41	5.71
5	341.50	590.26	35.62	5	513.78	470.20	5.40
6	348.14	593.18	34.24	6	514.78	459.67	5.10
7	354.62	595.90	32.88	7	515.82	448.82	4.80
8	360.94	598.44	31.56	8	517.02	437.74	4.52
9	367.06	600.81	30.26	9	518.42	426.46	4.26
540	373	603	29	580	520	415	4
1	378.78	605.02	27.76	1	521.68	403.36	3.76
2	384.38	606.91	26.54	2	523.55	391.50	3.52
3	389.80	608.68	25.36	3	525.60	379.46	3.30
4	395.05	610.28	24.20	4	527.78	367.30	3.07
5	400.15	611.64	23.06	5	529.92	355.07	2.86
6	405.12	612.68	21.96	6	531.86	342.88	2.66
7	409.98	613.29	20.90	7	533.46	330.83	2.48
8	414.73	613.40	19.90	8	534.55	318.97	2.31
9	419.40	612.97	18.92	9	535.06	307.36	2.15
550	424	612	18	590	535	296	2
1	428.50	610.54	17.12	1	534.44	284.89	1.87
2	432.89	608.56	16.28	2	533.34	274.08	1.75
3	437.16	606.01	15.48	3	531.64	263.58	1.65
4	441.33	602.96	14.74	4	529.40	253.40	1.55
5	445.44	599.46	14.02	5	526.72	243.47	1.46
6	449.51	595.60	13.34	6	523.69	233.74	1.38
7	453.59	591.47	12.72	7	520.44	224.18	1.30
8	457.69	587.15	12.12	8	517.05	214.70	1.20
9	461.83	582.66	11.54	9	513.58	205.30	1.10
560	466	578	11	600	510	196	1
1	470.18	573.13	10.49	1	506.26	186.84	0.89
2	474.44	568.08	10.01	2	502.42	177.80	0.77
3	478.76	562.88	9.57	3	498.47	168.90	0.64
4	483.11	557.50	9.16	4	494.40	160.16	0.50
5	487.40	551.84	8.76	5	490.10	151.58	0.37
6	491.54	545.84	8.38	6	485.46	143.26	0.24
7	495.42	539.41	8.03	7	480.41	135.21	0.14
8	498.98	532.47	7.68	8	474.82	127.47	0.06
9	502.17	525.00	7.34	9	468.68	120.07	0.02

TABLE 5. (*Continued*)

λ in mμ	ρ_0	γ_0	β_0	λ in mμ	ρ_0	γ_0	β_0
6.0	462	113	0	640	195	10	0
1	454.85	106.24	0.00	1	186.49	8.82	0.00
2	447.18	99.81	0.00	2	178.09	7.77	0.00
3	439.00	93.69	0.00	3	169.83	6.86	0.00
4	430.34	87.89	0.00	4	161.72	6.06	0.00
5	421.35	82.39	0.00	5	153.78	5.38	0.00
6	412.12	77.19	0.00	6	146.08	4.79	0.00
7	402.78	72.26	0.00	7	138.62	4.26	0.00
8	393.45	67.59	0.00	8	131.44	3.80	0.00
9	384.19	63.18	0.00	9	124.57	3.38	0.00
620	375	59	0	650	118	3	0
1	365.85	55.08	0.00	1	111.72	2.67	0.00
2	356.74	51.42	0.00	2	105.74	2.37	0.00
3	347.73	48.01	0.00	3	100.08	2.12	0.00
4	338.79	44.84	0.00	4	94.72	1.90	0.00
5	329.92	41.88	0.00	5	89.64	1.70	0.00
6	321.05	39.09	0.00	6	84.82	1.54	0.00
7	312.16	36.43	0.00	7	80.28	1.40	0.00
8	303.17	33.87	0.00	8	75.96	1.25	0.00
9	294.12	31.40	0.00	9	71.87	1.12	0.00
630	285	29	0	660	68	1	0
1	275.86	26.69	0.00	1	64.36	0.89	0.00
2	266.72	24.45	0.00	2	60.95	0.77	0.00
3	257.57	22.28	0.00	3	57.78	0.66	0.00
4	248.42	20.16	0.00	4	54.82	0.53	0.00
5	239.32	18.14	0.00	5	52.04	0.41	0.00
6	230.26	16.22	0.00	6	49.43	0.30	0.00
7	221.28	14.43	0.00	7	46.93	0.20	0.00
8	212.40	12.80	0.00	8	44.55	0.12	0.00
9	203.64	11.32	0.00	9	42.24	0.05	0.00
				670	40	0	0

Fig. 1 illustrates the smoothness of the interpolated values obtained by this method; it shows a portion of the ρ_0 curve near its maximum which possesses an irregularity of such nature that graphical interpolation is difficult.

It is to be noted that the interpolation has not been carried out beyond the limits 410 and 670 mμ; this serves to emphasize that the present plan is to refrain from using the interpolated values in obtaining

the trilinear coordinates corresponding to a given spectral distribution of energy. There would now seem to be little need to make use of intervals smaller than 10 mμ for this purpose although advances in colorimetric technique may be made in the future which will require smaller intervals to be used. The interpolation of the O. S. A. curves by a somewhat refined method does not presuppose this advanced technique; it is merely a question of adopting arbitrarily some one of the many equally reliable interpolations so that computed results via the O. S. A.

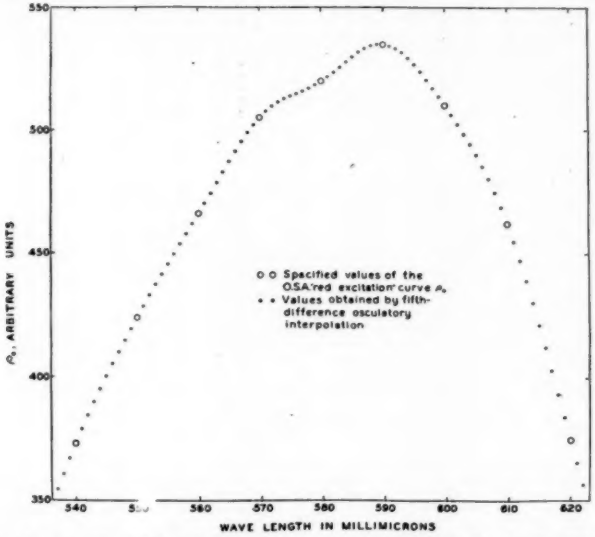


FIG. 1. *An example of interpolation of the O. S. A. "excitation" data by the fifth-difference, osculatory formula.*

A portion of the red curve near its maximum is chosen for a demonstration of the smoothness of the interpolated values.

"excitation" data which depend on interpolation may be perfectly intercomparable; the specific purpose, as previously stated, is to make possible the computation of rigorously comparable values of dominant wave length and colorimetric purity from given values of trilinear coordinates. The interpolated results given in Table 5 are sufficient to permit reproducible interpolation for dominant wave length to tenths of a millimicron merely from a table of values. If, for special purposes, a comparison of values to hundredths of a millimicron be desired it is probable that an interpolation graph based on the values of Table 5 would afford an adequate basis. It may be pointed out, too, that interpolations of any precision desired, however great, may be accomplished by carrying the appropriate number of decimal places in computing by the formula.

THE APPLICABILITY OF PHOTOELECTRIC CELLS TO COLORIMETRY

By Herbert E. Ives and E. F. Kingsbury

[Bell Telephone Laboratories, New York, N. Y. Received March 21, 1931]

Introduction

The possibility of using some form of radiometer as a substitute for the eye in photometry has been a long standing dream. The ideal instrument for this purpose may be postulated as one which upon exposure to an illumination indicates promptly, accurately, and infallibly the value of this illumination upon a direct reading scale. The modern laboratory voltmeter or ammeter represents the attainment, in another field of measurement, of the degree of accuracy and reliability which would be adequate for practical photometry. Such an instrument would be a definite improvement over the eye, since the latter is useless as an indicating instrument, and can be employed only by balance or substitution methods. This ideal instrument has not as yet proved capable of attainment, where the highest accuracy is desired, for the only photosensitive devices which are sufficiently sensitive for practical purposes, namely photoelectric cells, have exhibited faults in the nature of their response such as to force the use with them, in precision work, of substitution methods similar to those used with the eye. Nevertheless such gains in speed and simplicity of measuring routine have proved possible even with these limitations as to have made the photoelectric cell an instrument of real utility in photometry.

When it comes to one of the most difficult and exacting branches of photometry, namely, colorimetry, the photoelectric cell has long been out of the question because of the limitation of its sensitiveness to a restricted part of the visible spectrum, namely, the blue end. This particular limitation has, however, with the past few years, been removed, due to the development of new kinds of photoelectric cells, sensitive to the entire visible spectrum. Cells consisting of alkali metals specially treated by exposure to hydrogen, oxygen, or sulphur vapor, and subjected to various more or less empirical and obscure processes, can now be produced responsive to practically any part of the visible, the ultraviolet or near infrared, to any relative degree desired. With these new developments in photoelectric cells, the primary obstacle to their use in color measurement has been removed, and various instruments have been experimented with and developed to an ostensibly commercial stage

in which color sensitive photoelectric cells are used with the intention of making possible the measurement of color by an entirely physical procedure.

It is the purpose of this paper to consider critically the requirements for a precision physical colorimeter, and to estimate, in the light of a large body of experimental data on the new types of photoelectric cells, to what degree the requirements for physical colorimetry may be met at the present time. The paper is intended to be very specifically limited to the problems of precision color measurement, and it is assumed that the reader is already acquainted with the principal facts relating to photoelectric cells and their use in ordinary photometric measurements, in which no pronounced color differences are faced. Our study does not concern itself with certain problems of sorting and selection, commonly spoken of as "color" measurement, in which the nature of the colors concerned and their range of deviation from certain standards are known in advance, thereby greatly simplifying the problem.

VISUAL METHODS OF COLOR MEASUREMENT

Three general methods exist for the measurement of color by visual means:

1. Trichromatic matching

In this the color in question is exactly matched in appearance by a mixture of three chosen primaries, red, green and blue, and the measurement is expressed in terms of the relative proportions of the three primaries on some convenient scale, such as one in which the amounts of the primaries to match white are each called unity.

2. Measurement by hue, luminosity and purity matching

In this a mixture of a spectrum color and white is found which again gives an exact visual match with the color to be measured. The luminosity of the color, and of the white which is mixed with the band from the spectrum, are then separately measured and the complete measurement is again expressed in terms of three variables.

3. Spectro-photometric analysis

In this method, speaking strictly, no question of color really enters. The measurement is one of relative radiant intensity at a large number of wave lengths, and the measurement is recorded either in a table of values, or in a curve of relative intensities, with wave lengths as the

abscissae. Spectro-photometric values can be reduced to trichromatic values by the use of color mixture curves of the spectrum for any given set of primaries, and through these in turn to hue, luminosity and purity. Unlike the first two methods, spectro-photometric data are in general independent of the character of vision of the observer or of the quality of the illumination under which the observations are made. They constitute a complete record, but must be interpreted before they have a meaning in terms of color.

PHYSICAL METHODS OF COLOR MEASUREMENT

Of these three methods of color measurement, the second, namely, hue, luminosity, and purity matching, is not susceptible of reduction to a physical basis, since the match which is made between the mixture of a spectrum band and white is entirely subjective. This leaves methods one and three as the only possibilities for physical methods. Method one, namely, trichromatic matching, is theoretically entirely suitable for reduction to a physical process. The mixture curves of the spectrum may be considered as templates, transmitting, at each wave length, the amount of the radiation which can be replaced by that of a primary to reproduce the color. A physical trichromatic color analyzer will then consist of means for transmitting to the light sensitive device, three bands of the spectrum in the proportions of the mixture curves at each wave length. It is obvious that the photosensitive device to be used in such an instrument must not only be sensitive throughout the visible spectrum, but must have a strictly proportional response to light intensity, and must for practical purposes be of constant and reproducible wave-length response. Given these characteristics combined with adequate sensitiveness, trichromatic physical color analysis would appear to be the simplest and most convenient method of color analysis. An experimental instrument of this sort, using a thermopile, was devised and was reported some years ago, whereby the principle of the method was demonstrated.[1] The sensitiveness of the thermopile is, however, altogether too small for practical color measurement, and further progress along this line is dependent on the discovery or development of appropriate light sensitive devices. We may anticipate our discussion of photoelectric cells at this point to state that they are at the present time very far indeed from possessing the characteristics above listed which are essential for their use in this kind of color measurement.

[1] Ives, *A Precision Artificial Eye*, Phys. Rev. *6*, (5), 334; 1915.

Proceeding now to a discussion of physical spectrophotometry or radiometry with photoelectric cells, we may call attention again to the ideal which has been referred to in connection with physical photometry in general; namely, an instrument which would indicate the desired values directly upon a scale. Were there available photoelectric cells which could read off directly the intensity values through the spectrum in an absolutely accurate and reliable manner, the problem of photoelectric spectro-photometry would be in a highly satisfactory state. Just as, however, it has been found in ordinary photoelectric photometry that the characteristics of the cells deviate too far from the ideal to make this possible for the most precise work, so in spectrophotometry we have considerable experimental evidence that the only method which may now be entertained is the balance or substitution method. This is peculiarly true of the recently developed color sensitive photoelectric cells. Due to the elaborate processes used in order to make them color sensitive, they are subject in their present stage of development to a variety of uncertainties and deviations from reliability. In order to make this abundantly clear, we present, in the form of a list with illustrative figures and brief comments, the various deviations from the ideal which may be expected in color sensitive photoelectric cells of the more recent types.

CHARACTERISTICS OF PHOTOELECTRIC CELLS OF IMPORTANCE IN SPECTRO-RADIOMETRY

The illumination-current relationship

This is, of course, a fundamental characteristic which must be known for any use of the cell. The most desired relationship is a strictly rectilinear one, and it is generally held that an ideally constructed and operated cell would exhibit a strict proportionality between the photoelectric current and the illumination. It may be stated, however, as a general condition, that strict linearity is never found in practical cells. In vacuum cells, the approach is probably nearest, provided the clean glass surfaces such as window and stem are kept very small, and as far as possible from the illuminated area. In gas-filled cells deviations from linearity become noticeable as the ionization voltage of the gas is approached. The manner in which the illumination-current relationship is affected by the voltage on the cell is shown clearly in Fig. 1 where data are shown for a potassium-hydride cell, in which there is no noticeable variation at 90 volts, and for a caesium-oxide cell in which the

relationship is apparently linear at 22-1/2 volts, but very decidedly curved at 90 volts. The illumination-current relationship depends not only on the voltage but also on the level of illumination. Thus at 90 volts, the caesium-oxide cell shown seems to be very linear at low illuminations, with a rather critical value, dependent on the cell, at which a pronounced curvature starts. Besides general curvature of the

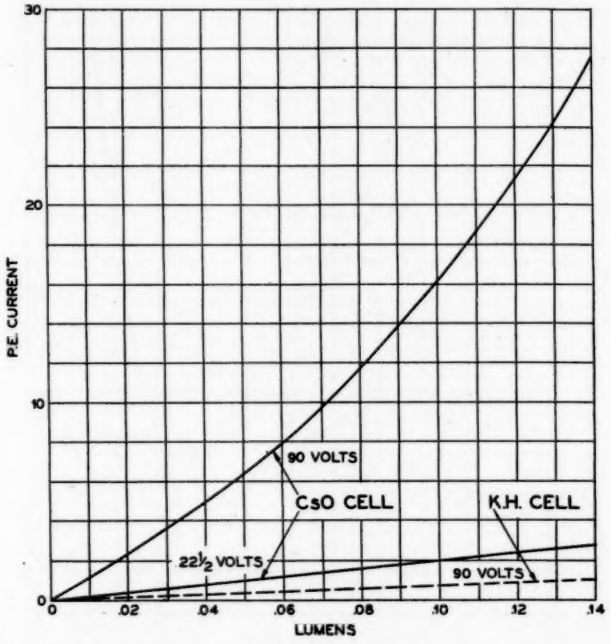


FIG. 1. *Illumination-current response of a potassium-hydride and a caesium-oxide cell.*

characteristic, such as is here shown, careful measurement usually reveals small local irregularities, whose nature and cause is obscure, but which are great enough to make a bar to really high accuracy in measurement.

An important factor in the practical set-up with any photoelectric cell is the series resistance which is used, either for protective purposes, or in order to provide a voltage drop for amplification purposes. The effect of a series resistance is to drop the voltage across the cell by an amount proportional to the current passed. In vacuum cells, (Fig. 2) this voltage drop, if one is working in the region of current saturation,

causes no drop in current, but with gas-filled cells, operated near the ionization voltage, at which there is always an urge to work the cell in order to secure large currents, this drop may be considerable. The char-

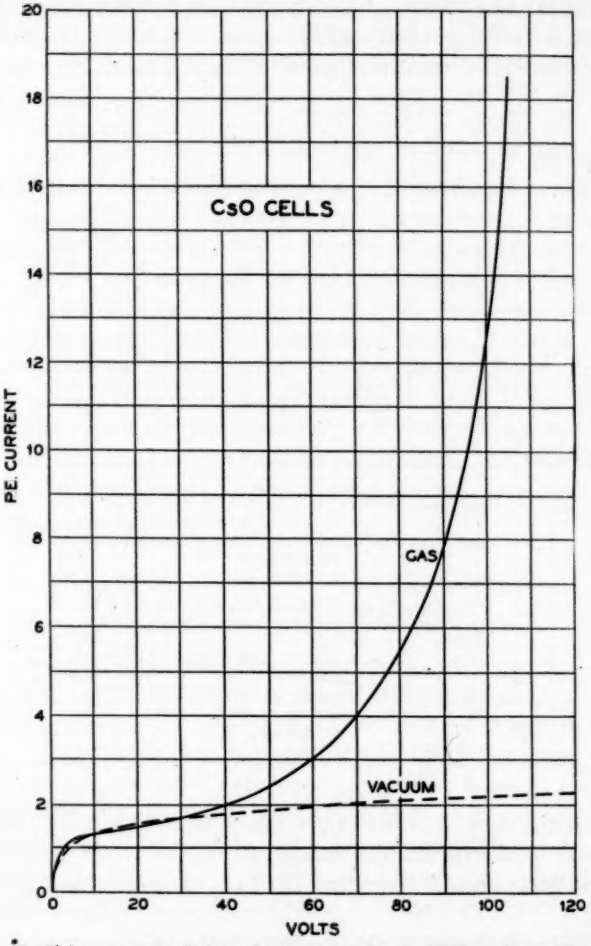


FIG. 2. *Voltage-current relations of a vacuum and a gas-filled caesium-oxide cell.*

acteristic effect of high series resistance is to bend the illumination-current curve downward toward the illumination axis, as shown by the experimental data of Fig. 3. In the case given a cell is used which exhibits initially an upward curvature similar to that exhibited in Fig. 1.

This is transformed by the introduction of series resistance through an "*S*" shape into a downward curvature.

Other more obscure effects have been observed in highly sensitive cells, among which we may record an effect dependent on the time of exposure, which is indicated in Fig. 4, where a temporary shift in the

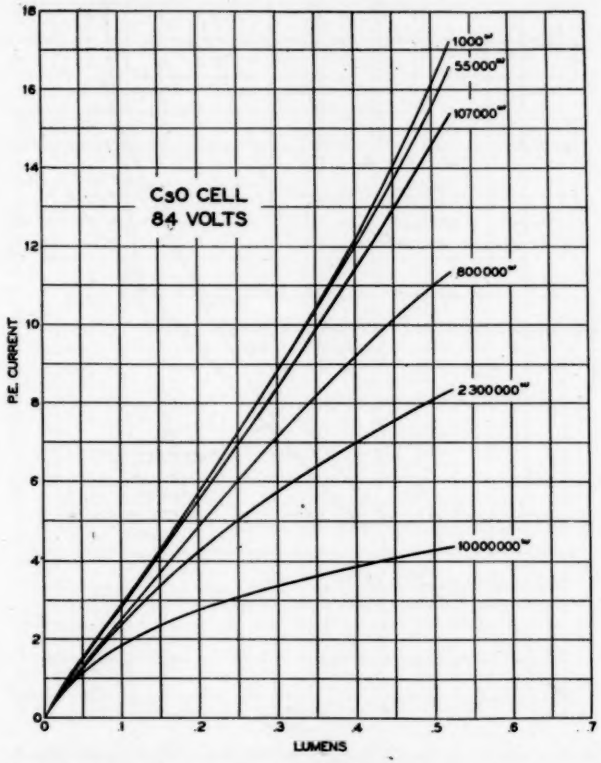


FIG. 3. *Effect of different series resistances on the illumination-current response of a caesium-oxide cell. Constant battery voltage.*

response occurs during the first few minutes after the light is turned on. This effect may result in either an enhancement or a falling off of the sensitivity. The evidence indicates that it is due to an alteration of the cathode surface by the gas bombardment and is more or less reversible after the ionization has ceased. Another effect noted in potassium-halide cells and shown in Fig. 5 is an inhibition of response under illumi-

nation by one color if light of another color falls on the cell.[2] An effect of this sort would be particularly disastrous where wide spectral bands are used, as in the trichromatic method of measuring. It is of importance in spectro-photometric applications, in that the measurement may

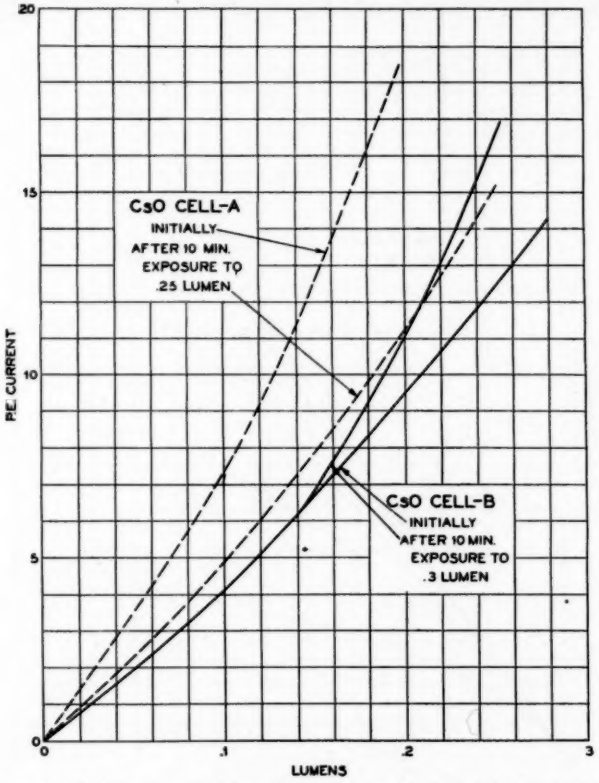


FIG. 4. *Variation in sensitivity of two caesium-oxide cells while illuminated.*

take place in a region of the spectrum where the inhibiting effect alters the illumination-current relationship. This inhibiting effect appears also to be a slow one, and may possibly contribute to the variation of response with time already noted.

THE SPECTRAL RESPONSE CURVE

It is of great practical importance that the spectral response curve of the cell be as definite, constant, and reproducible as possible. The color

[2] Olpin, *Inhibition of Photoelectric Emission by Near Infrared Light*, Phys. Rev. *36*, 376; 1930.

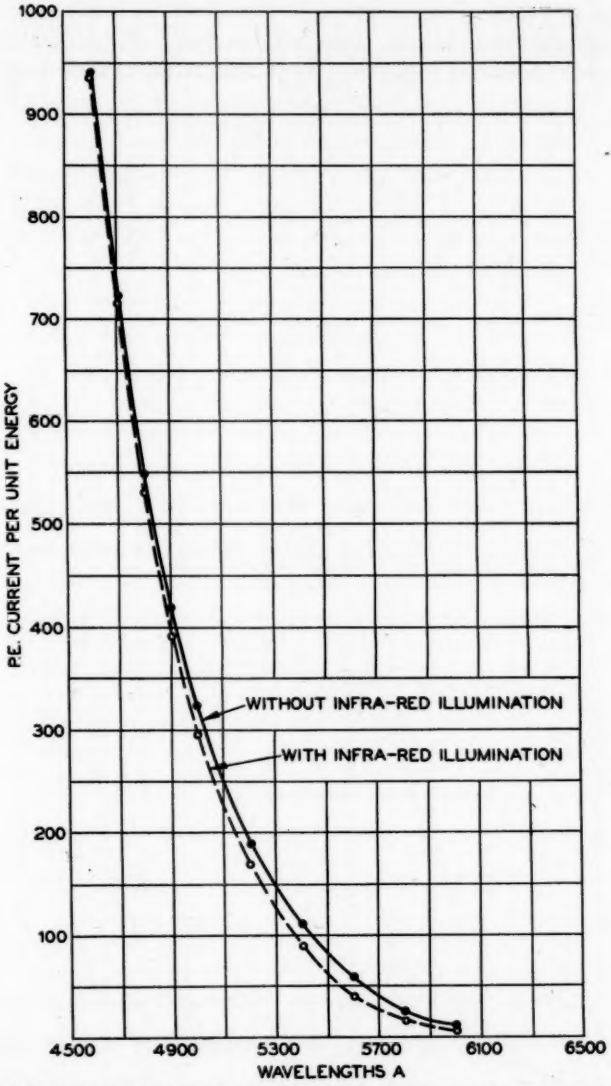


FIG. 5. *Variation in spectral sensitivity produced by simultaneous irradiation with infrared light. Potassium cell treated with bromine.*

sensitive photoelectric cells are far from satisfactory in this respect. While the general character of the spectral response curve for any one

material and method of treatment is characteristic, it has not yet been found possible to duplicate these with anything like accuracy nor to insure their constancy with time. As an illustration of these statements,

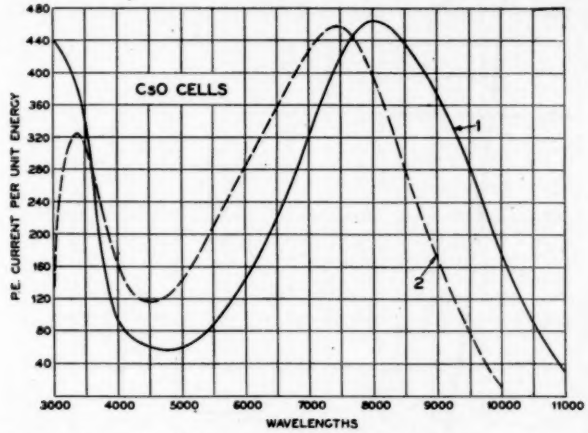


FIG. 6. *Differences in sensitivity of two caesium-oxide cells throughout an equi-energy spectrum.*

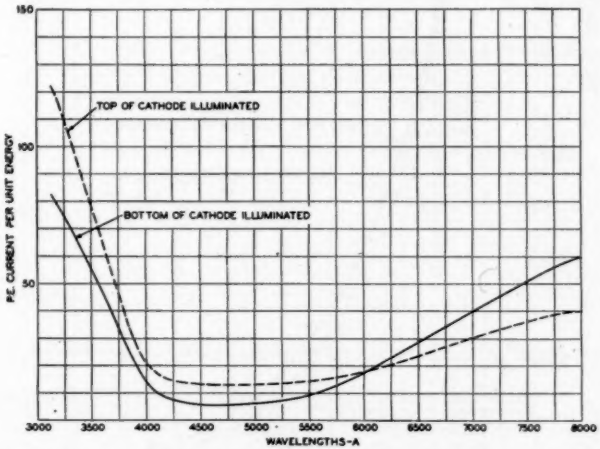


FIG. 7. *Variation in spectral sensitivity over the cathode surface of a caesium-oxide cell.*

there are shown in Fig. 6 spectral response curves for two caesium-oxide red sensitive cells given presumably quite similar treatment in manufacture. Fig. 7 shows the differences in sensitiveness between two spots, at the top and bottom respectively, of the cathode of a similar cell.

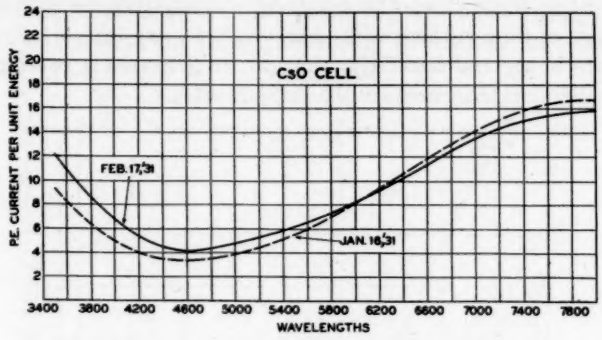


FIG. 8. *Change in spectral sensitivity with time, in a caesium-oxide cell.*

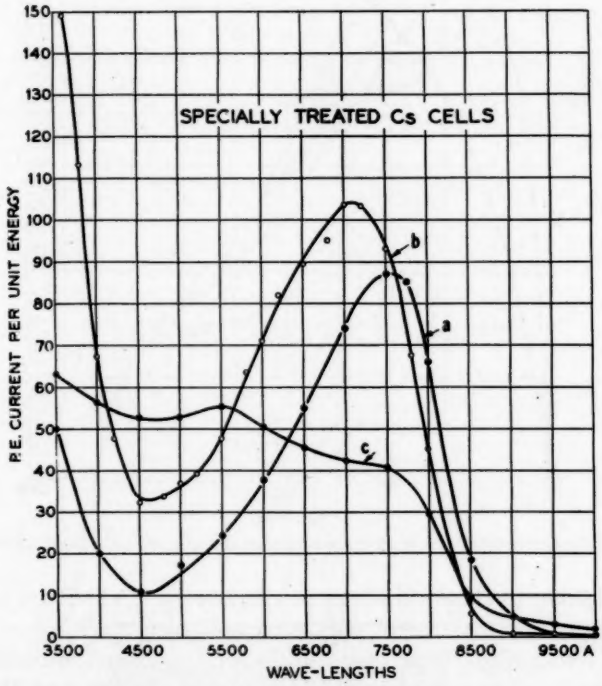


FIG. 9. *Relative sensitivity throughout an equi-energy spectrum of some caesium-oxide photoelectric cells with different treatments of the cathode surface.*

In Fig. 8 are shown characteristic changes in sensitiveness such as occur with lapse of time in these cells. Fig. 9[3] gives some typical cases of the variations in spectral sensitivity that can be produced in caesium-oxide cells by different treatments of the cathode surface.

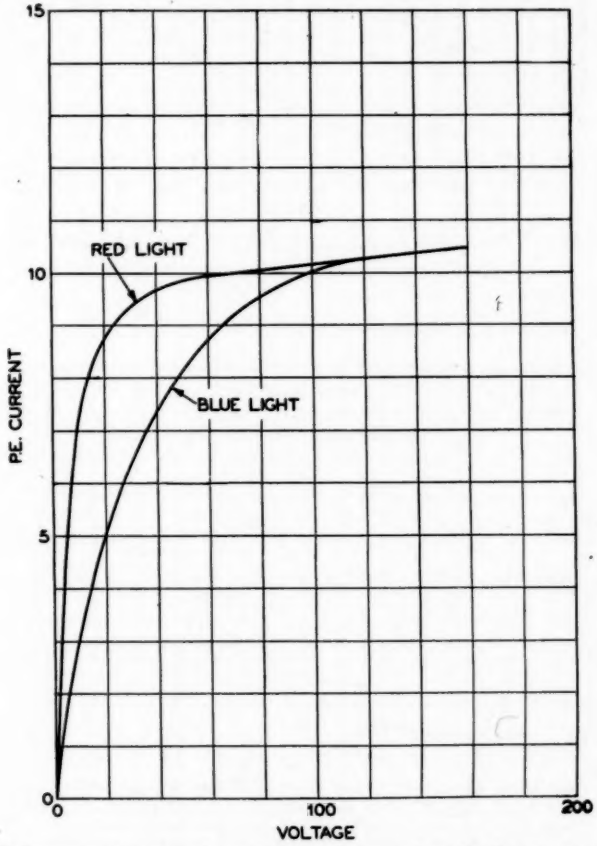


FIG. 10. *Voltage-current response of a vacuum potassium central anode cell with red and blue light.*

In addition to these variations of characteristic, which are encountered in the specially treated cells, there are other factors affecting the relative response to different parts of the spectrum which are dependent upon the fundamental phenomena of photoelectricity and the geo-

[3] Olpin, *Method of Enhancing the Sensitiveness of Alkali Metal Photoelectric Cells*, Phys. Rev. *36*, 251; 1930.

metrical construction of the cell. Thus Fig. 10 shows voltage-current curves for long wave and short wave energy in central anode cells of the

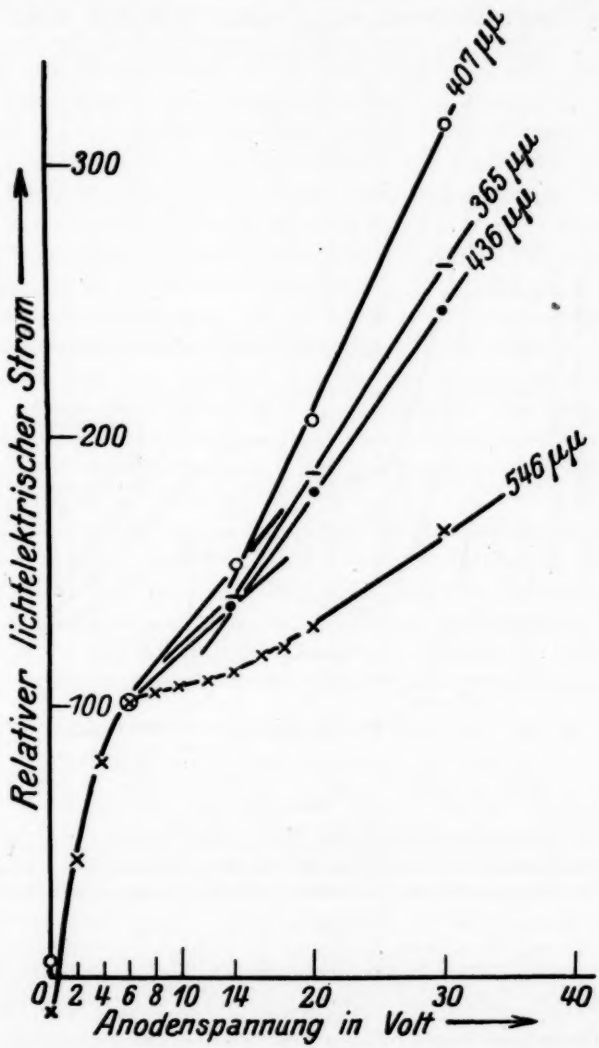


FIG. 11. *Voltage-current response of a gas-filled central anode cell at different wave lengths according to Fleischer and Goldsmith.*

vacuum type.[4] In these, due to the higher velocity of the short wave electrons, saturation is slower of attainment. Attention may also be called to a phenomenon recorded by Fleischer and Goldsmith;[5] namely that on exact analysis with monochromatic light, it is found that the

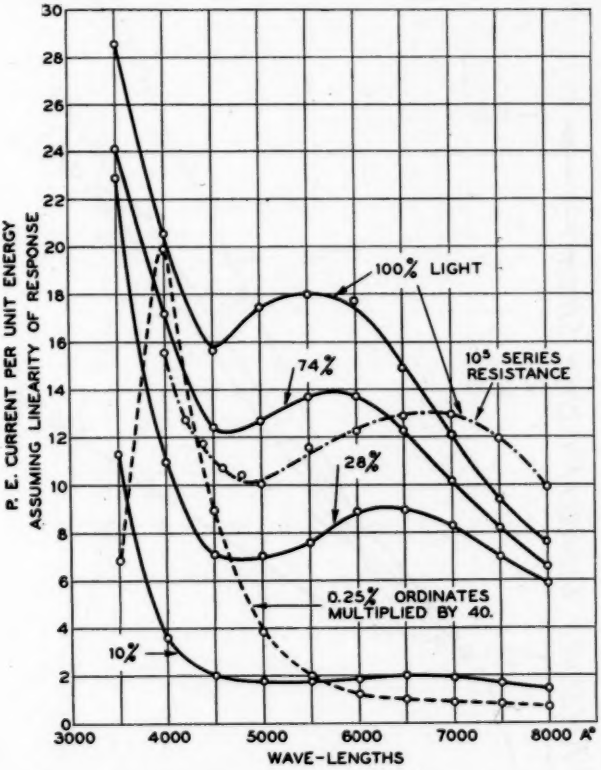


FIG. 12. *Spectral response characteristics at various illuminations of a caesium thin film cell having a photo-sensitive, high resistance window. Full and dashed curves taken with electrometer across 560 Ω resistance. Dot and dashed curves taken with galvanometer of 100,000 ohms resistance.*

voltage-current curves in gas-filled cells are different in slope throughout their whole extent for different colors (Fig. 11). All phenomena of

[4] *The Voltage Current Relation in Central Anode Photoelectric Cells*, Ives and Fry, Astrophy. J., July, 1922.

[5] *Uber Charakteristiken von Alkalizellen und ihre Bedeutung für die lichtelektrische Messmethode*, Physik ZS., *29*, 691; 1928.

this sort mean, in terms of the spectral response curves, that *these are dependent upon the exact voltage used.*

We conclude our discussion of the vagaries of spectral response curves by giving data on a commercial thin film caesium cell of the vacuum type, the exact method of manufacture of which is unknown to us, which is of high intrinsic sensitiveness, but which exhibits an extraordinarily complex behavior. In this cell the glass window is photosensitive with a different spectral response from the cell wall coating. Owing to the very high resistance of the window coating the illumination-current relationship of the part of the current contributed by it is far from linear, and, in addition its contribution to the total current varies with the circuit conditions. A spectral response curve taken with high illumination, using a galvanometer of only 100,000 ohms resistance is shown by the dot and dashed curve Fig. 12. Curves taken with an electrometer, measuring the potential drop across a series resistance of 560 megohms are shown for a series of illumination, ranging from that used with the galvanometer down to 0.25% of that value. The most superficial examination reveals that these curves, all obtained from one cell, show a range of characteristics as extreme as those normally shown by cells of entirely different cathode materials.

It should be sufficiently clear in view of all these effects which alter the relative response to different colors that any instrument which is designed upon the assumption of a definite or constant spectral response curve as, for instance, by the incorporation of spectral templates, is confronted with a practically impossible handicap, unless or until considerably greater mastery of photoelectric cell characteristics is attained.

CONCLUSION FROM STUDY OF ILLUMINATION-CURRENT AND SPECTRAL RESPONSE CHARACTERISTICS

The conclusion which is to be drawn from the data above presented, is obvious to anyone familiar with the technique of exact measurement. This is that any direct reading method, with photoelectric cells now available, sensitive throughout the visible spectrum, is out of the question where any high accuracy is required. As in the case of the eye, photometric precision is only to be attained where a substitution or balance method is used, with sufficient quickness of alternation of the two stimuli and proper optical conditions for minimizing the effect of the alternation.[6]

[6] An optically ideal method for eliminating the dividing edge between two fields is that use in the polarization flicker photometer (Phil. Mag., April, 1917, p. 360).

CONSIDERATIONS ON CHOICE OF TYPE OF CELL

A practical problem in photoelectric spectro-photometry is the choice of the type of cell best fitted for the purpose. The first impulse is, of course, to pick the cell which is intrinsically most sensitive, and, in view of the fact that early cells were insensitive to the red end of the spectrum, to conclude at once that the most red sensitive cells, namely, the caesium cells, must be chosen. In practice, however, the character of the light source which is used and the nature of the apparatus employed for producing a spectrum must be given consideration. The pre-

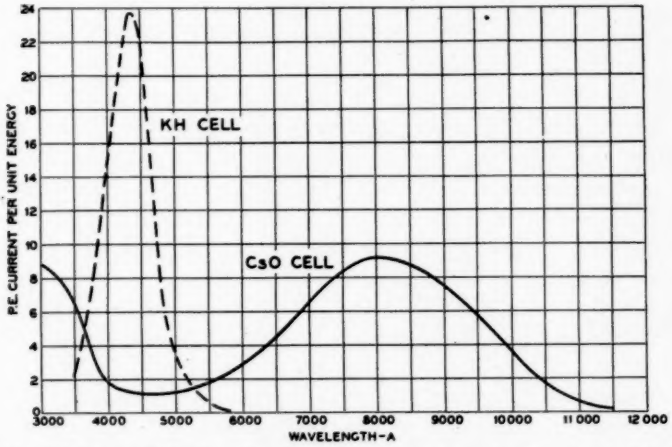


FIG. 13. *Relative sensitivity throughout an equi-energy spectrum of a potassium-hydride and a caesium-oxide cell at 90 volts.*

ferred scientific method of representing the spectral response curves is, of course, in terms of photoelectric current per unity energy through the spectrum, and we have presented the data in this form. However, it must be remembered that when a tungsten lamp is used as a light source, together with a prism instrument for dispersing the light, there is an enormous enhancement of the energy available at the long wave end of the spectrum. This is illustrated by comparison of Figs. 13 and 14 in which the potassium-hydride and caesium-oxide cells are compared, first on the basis of equal energy, and second on the basis of the energy distribution in the tungsten lamp, and, in Fig. 15 where the caesium-oxide cell is again shown with equal energy, with a tungsten lamp, and a tungsten lamp with its energy dispersed by a prism. It will be noted

that the caesium cell, in spite of its intrinsically greater sensitiveness to tungsten light, actually gives much smaller useful response through an important part of the visible spectrum than does a potassium-hydride cell. Other types[3] of cells are shown on a comparative basis in Figs. 16

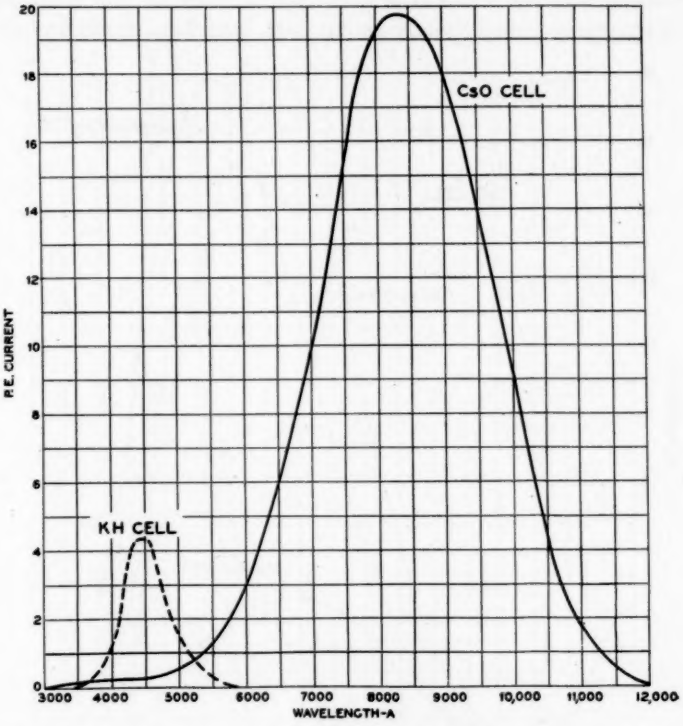


FIG. 14. *Relative spectral sensitivity to tungsten light 2710° K color temperature of the potassium-hydride and the caesium-oxide cell shown in Fig. 13.*

and 17, while it is evident from Fig. 18 that a thin film of caesium treated with sulphur gives measurements which are more convenient than any of the other types noted. The experimental sodium cell treated with Kryptocyanine shown in Fig. 17 would also be an excellent cell in this respect. This suggests the likelihood that the use of several cells, each for different parts of the spectrum, may be a useful artifice, which would have an additional advantage, in that errors due to scattered light of different wave length would be somewhat reduced

in the manner that color filters have been found of value in visual spectro-photometry.

DISCRIMINATING POWER OF PHOTOELECTRIC CELLS

Another question which is of fundamental technical and great popular interest—in view of many claims that have been made for photo-

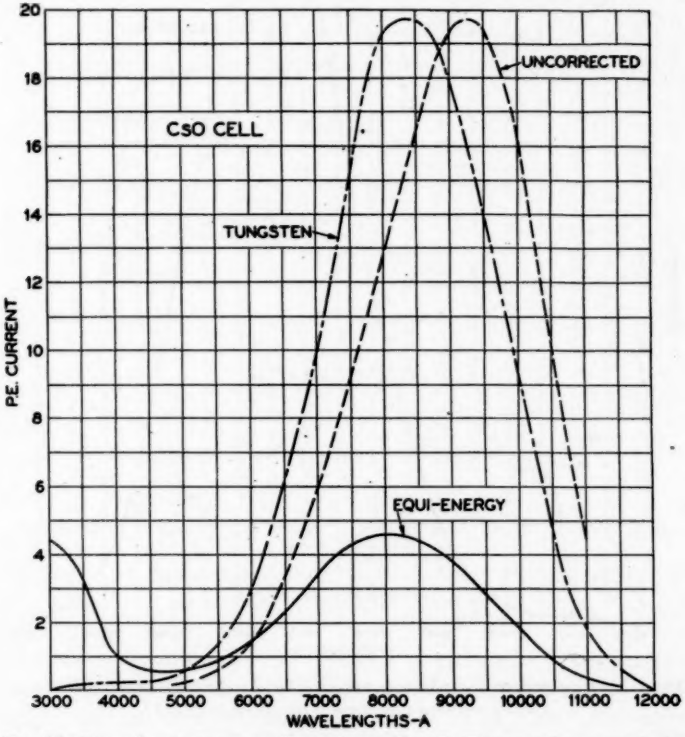


FIG. 15. *Spectral response curves of a caesium-oxide cell. Uncorrected curve as obtained by a prism spectrometer; tungsten curve corrected for dispersion of the spectrometer, but not for the energy distribution of the lamp at 2710° K color temperature; and equi-energy corrected for both.*

electric photometers—is the degree of discrimination which is possible with a photoelectric spectrophotometer. Specifically, is a photoelectric cell capable of detecting smaller intensity differences than is the eye? The answer to this question is a complicated one, and must be approached with circumspection. In the case of spectro-photometry we must have information on the amount of light coming from the surface

under measurement, which is determined by available light sources; and on the slit widths which are permissible by acceptable criteria. The photoelectric currents initiated by the stimuli so conditioned may then

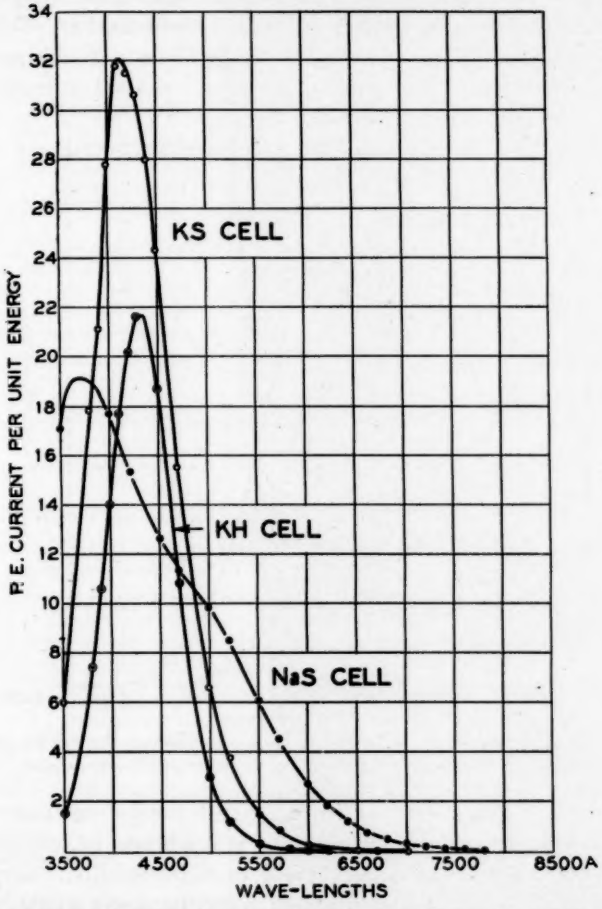


FIG. 16. *Relative sensitivity throughout an equi-energy spectrum of potassium-hydride, potassium-sulphur vapor and sodium-sulphur cells.*

be studied with reference to various available current measuring instruments.

As possible working conditions let us assume a white reflecting surface on which is focused the image of a tungsten filament, the spot of

light thus formed then being reimaged on the slit of the spectro-photometer. Let us assume the slits of the instrument to be each 100 Angstroms wide. (The necessary fineness of slit will vary with the nature of the color being measured.) Test measurements show that, with the most sensitive photoelectric cells, the currents obtained are of the order of 10^{-9} amperes. Now a sensitive electrometer will, without great difficulty, indicate by the "steady deflection" method, currents of the

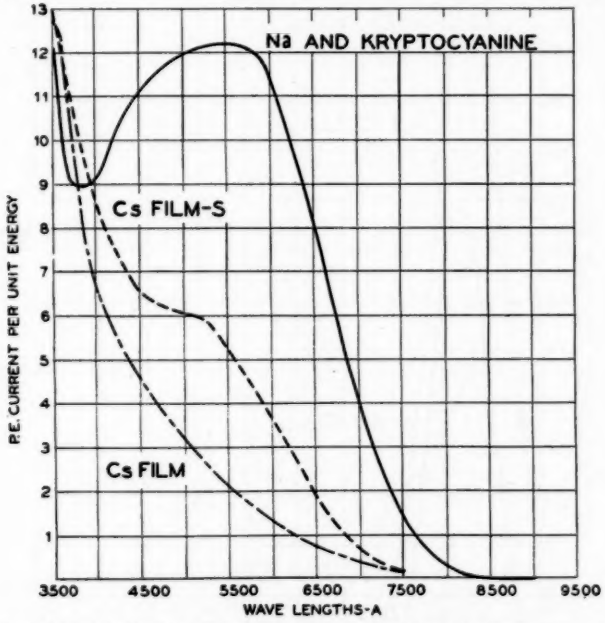


FIG. 17. *Sensitivity throughout an equi-energy spectrum of caesium thin film, caesium thin film on magnesium plus sulphur vapor and sodium treated with krypto-cyanine.*

order of 10^{-14} amperes. Consequently two "white" surfaces successively presented to the system, differing in brightness by only one part in $10^{-9}/10^{-14} = 10^{-5}$ should be capable of differentiation. Very dark surfaces, of the order of 2 or 3 percent reflecting power would, according to this analysis still be discriminated better than the approximately 1 percent capacity of the eye. It appears therefore that under the conditions specified, the photoelectric cell can exceed the eye in discrimination. It must be emphasized however that the attainment of this accuracy of measurement presupposes extreme steadiness of the light source, an absolutely smooth optical transition between test and com-

parison fields, a very small leakage in the photo-cell and a steady electrometer, preferably a very quick acting one, such as a string instrument. It is a strictly precision laboratory type of measurement;—inherently slow, and requiring skilled manipulation. Its real advantage over visual spectro-photometry, all factors taken into account, is apt

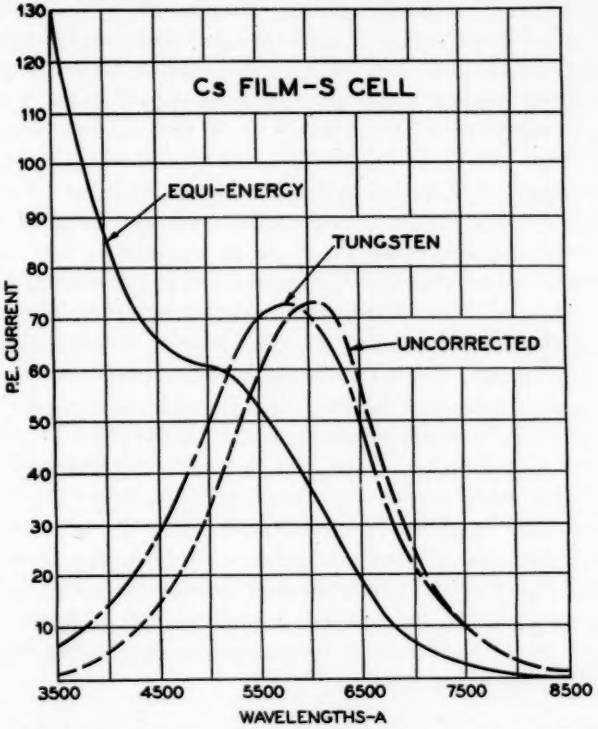


FIG. 18. *Spectral response curves of a caesium thin film cell treated with sulphur. Uncorrected curve as obtained by a prism spectrometer; tungsten curve corrected for dispersion of the spectrometer but not for the energy distribution of the lamp at 2710° K color temperature; and equi-energy corrected for both.*

to be chiefly in the possibility of extending the measurements with equal precision to the ends of the spectrum, by the use of blue sensitive and red sensitive cells, such as the potassium-hydride and caesium-oxide types.

AMPLIFICATION OF PHOTOELECTRIC CURRENTS

A large part of the interest in photoelectric cells in colorimetry or spectro-photometry is undoubtedly owing to the fact that they may be

used with vacuum tube amplifying devices, with which nowadays many people are familiar. In regard to electrical amplification, two facts must be borne in mind, first, that the currents detectable by amplifying devices are, generally speaking, no smaller than can be detected by previous devices, such as electrometers; second, that the currents with which we are concerned in photoelectric spectrophotometry lie in the region where "noise" and other tube sources of interference, make amplification difficult and unreliable. The greater speed, and the control of power, as for recording devices, which amplifying means offer, are accordingly always in danger of being purchased at the cost of sensitivity and accuracy.

With regard to methods of amplification, we distinguish between direct current amplification and alternating current amplification. In general, the choice between these will be dictated by the method of spectro-photometry that may be adopted and the amount of amplification, stability and speed demanded of the system. These latter requirements however recommend alternating current amplification as the more suitable, and, interestingly enough from our standpoint, alternating current amplification fits in quite well with the rapid substitution method which our study of photoelectric cells appears to indicate as essential.[7] Much work has been done on ac amplifiers for use in picture transmission and television, where currents of the order of 10^{-9} amperes are successfully handled. In spectro-photometry the speed of alternation of the two fields can be of the order of 100 cycles per second, or less, in place of the many thousands required for television. This means that series resistances can be increased a hundred-fold or more, with the same methods of amplification, thus promising satisfactory discrimination for the present purpose.[8]

CONCLUSION

The data presented in this paper, and the various comments and conclusions which have been drawn, we believe, furnish information of some value on the applicability of photoelectric cells[9] to color measure-

[7] An outstanding advantage of alternating exposure and alternating current amplification is that leakage currents and thermionic currents (which are of measurable magnitude at room temperature with some caesium cells) are blocked from the measuring system.

[8] The need for a smooth transition between the two fields under comparison is again to be emphasized in this connection. A finite dividing line will introduce an alternating current which sets a lower limit to sensitivity.

[9] See also Sewig, *Die lichtelektrische Zelle als Messinstrument*, ZS. für Instrumentenkunde, *50*, 426; July, 1930. This paper contains many useful references.

ment, or more specifically to spectro-photometry. We wish, however, to emphasize that the whole answer to the satisfactory performance of photoelectric spectro-photometers is by no means covered by these points. The attainment of accuracy and reproducibility in photometric instruments is dependent to a major degree upon the soundness of the optical arrangements employed, and the control of the illuminations used. In other words, a photoelectric cell instrument might use the photoelectric cell strictly according to the limitations which have been stressed above, but might still be inaccurate and unreliable for the same reasons that a poorly designed visual instrument would be. The substitution of an electric for a human eye is no panacea. Furthermore the very large questions concerned with the direction and nature of the illumination of the test surface; characteristics such as specular reflecting power, sheen, and so on, are in no way solved in the substitution of physical for visual observation. The future use of physical methods of color measurement is dependent not alone on the perfection of photoelectric cells, but on the development of general colorimetric methods; on the choice of conventions as to measuring conditions, and a clear understanding on the part of users, of the fact that color alone does not completely describe many of the most important characteristics of "colored" surfaces.

Committee on Award of Ives Medal.—In this Journal *21*, 448, July, 1931, the Committee on Award of the Frederic Ives Medal was incorrectly given. The Committee consists of:

GEORGE B. PEGRAM, *Chairman*
L. T. TROLAND
E. C. CRITTENDEN
C. E. K. MEES
A. H. PFUND.
L. B. TUCKERMAN,
Secretary.

SPECTROPHOTOMETRY AT THE BUREAU OF STANDARDS[1]

By K. S. Gibson

[Colorimetry Section, Bureau of Standards, Washington, D.C.

Received April 20, 1931]

I. Introduction

It is not attempted herein to point out the importance of spectrophotometry as applied to colorimetric analysis and specification or as used in chemical and industrial research. Such has previously been done many times and will doubtless be clearly indicated in some of the papers on the present program. Nor will any discussion or résumé, historical or otherwise, be given of apparatus or methods of spectrophotometry in general. The subject has been more or less covered in this respect in two recent publications.[2]

The purpose of the paper is, rather, to note briefly the apparatus and methods used in the colorimetry section of the Bureau of Standards to obtain spectrophotometric data, and to describe the means there taken to avoid error and to insure accuracy in the values obtained. The four principal methods used—viz., the visual, photoelectric, thermoelectric, and photographic—have been described in detail elsewhere, so that no attempt is made to give complete descriptions here. Each method was developed for certain specific purposes. Each has certain advantages and certain limitations, which make it specially adapted for certain purposes and less adapted for others.

II. The Visual Method—Koenig-Martens Spectrophotometer

This apparatus is described in detail in a recent Bureau publication.[3] The spectrophotometer itself is a Schmidt and Haensch instrument, but the auxiliary equipment for holding and illuminating the samples was designed and constructed at the Bureau. The accompanying illustration is taken from RP 30 and illustrates some of the optical and structural features of the apparatus. These are further considered below.

[1] Paper presented at the special colorimetry session of the Optical Society of America, New York, February 26, 1931. Publication approved by the Director of the Bureau of Standards of the U. S. Dept. of Commerce.

[2] Report of O.S.A. Committee on Spectrophotometry, J.O.S.A. and R.S.I., *10*, pp. 169–241; February, 1925. K. S. Gibson, *The Use of the Photoelectric Cell in Spectrophotometry*, published in "*Photoelectric Cells and Their Applications*," pp. 157–173; June, 1930, by the Physical and Optical Societies, London.

[3] H. J. McNicholas, *Equipment for Routine Spectral Transmission and Reflection Measurements*, Bur. Stand. Jour. Research, *1* (RP 30), pp. 793–857; November, 1928.

The auxiliary equipment provides for both transmission and reflection measurements. It was designed and constructed for daily routine use and the various operations (change of source, insertion of sector, etc.) incidental to the measurement of different kinds of samples can be made and correct working alignment effected in a moment's time. The features which contribute to the precision and accuracy of measurement will be particularly noted.

The distinction between precision and accuracy cannot be too often emphasized. By precision is meant the reproducibility possible regardless of whether the results may be accurate or not. By accuracy is meant that the results truly represent the quantity which it is claimed is being measured; and with any apparatus the accuracy of the results is limited by the preciseness with which this quantity can be defined. The design of apparatus will, of course, depend on the nature of the quantity which it is desired to measure.

1. SPECTRAL TRANSMISSION MEASUREMENTS

Nearly all materials submitted to the Bureau for spectral transmission measurements are transparent materials, such as colored glass, or liquids that may be inclosed in cells with glass end plates. In general, it is required that such materials have plane, parallel, and polished surfaces and be free from obvious optical imperfections. Unless such is the case, the material is usually not accepted for standardization, although in certain cases samples that are optically imperfect, e.g., Lovibond glasses, are accepted for test.

It is for these classes of material that the Bureau apparatus was designed, viz., for optically perfect samples or those whose optical imperfections are not too serious. The transmission that is thus measured may be defined as the ratio of the intensities of the transmitted to the incident light, both in a direction at right angles to the surfaces of the specimen. The apparatus is not designed to measure the complete transmission of samples that considerably diffuse the incident light or to measure the transmission of lens or wedge shaped materials.

For the transmission measurements the totally reflecting prism (item 4 in Fig. 1) and the lenses (1 and 2) are out of the beam. The light from the source passes through the collimating lenses (3) and rhombs as shown in Fig. 1, one beam passing through the transmission sample as indicated. The two beams eventually form the halves of the circular photometric field of the Koenig-Martens spectrophotometer. The vertical dividing line of the field is produced by the edge of the biprism which

comprises part of the Wollaston prism unit. The brightnesses of the two halves of the field may be equalized by rotation of the nicol prism in front of the ocular slit. The dividing line practically disappears when the brightnesses are made equal, an essential condition if high precision is to be obtained.

The transmission sample may readily be shifted by means of a hand wheel and carrying mechanism from one beam to the other by the observer. The regular procedure is to take five readings of the nicol with

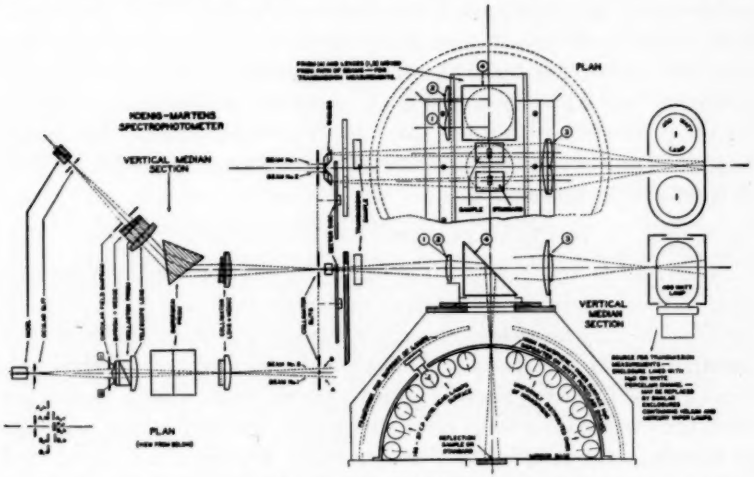


FIG. 1. *General arrangement of Koenig-Martens spectrophotometer and auxiliary equipment. (Uniform scale not used throughout the diagram.) This figure is taken from B. S. Res. Paper No. 30, Fig. 3, 1928.*

the sample in one beam, ten with it in the other beam, and five with the sample returned to its first position, making twenty readings in all. These readings, ten on each side, are recorded by the observer directly on an adding machine, the banks of which are split to take the two sets of readings separately. At the completion of the twenty readings, the averages are obtained immediately from the totals by merely shifting the decimal point. The use of the adding machine thus eliminates the labor of pencil-and-paper recording and the time otherwise necessary for averaging the readings. The publication noted above (RP 30) should be consulted for various details of construction and operation.

Three different types of lamps are in common use with the instrument, viz., incandescent, mercury, and helium. Each lamp (or pair of

lamps) is placed in a white-lined inclosure, the inner surface of which is formed by a deposit of magnesium oxide. The two beams of light forming the photometric field originate, not directly from the lamps, but from the rear diffusing surface of the inclosure. High brightness is obtained by making the area of the inclosing wall as small as possible.

The source of light, therefore, whether the incandescent, the mercury, or the helium lamps are being used, is an area of high and practically uniform brightness. This area is large enough to avoid the introduction of error due to thickness or minor optical imperfection of the sample or to slight unavoidable scattering of light by the sample. That is, for the type of sample ordinarily accepted for measurement, the source is, in effect, unchanged as the sample is introduced into the beam.

The use of the mercury and helium light serves two very important purposes:

1. Check of the wave-length calibration of the spectrophotometer in any region of the spectrum is possible at any time. Such check is always made at the beginning of any series of measurements unless the sample is known to have no considerable selectivity in its transmission. Further check of the wave-length calibration is often made during a set of measurements, this depending on the type of transmission and the importance of the measurements. There are several types of transmission curves where an error of half a millimicron in the wave-length setting will cause a considerable error in the transmission.

2. Values of transmission free from wave-length and slit-width errors may be obtained at certain wave lengths by using the homogeneous light to make the photometric settings. No matter how carefully the wave-length calibration is made or checked, there is always possibility of slight error in the wave length setting with the continuous-spectrum source. Furthermore, even though the wave-length setting be correct, the use of the necessary finite slit widths with the continuous-spectrum source may, through the resulting mixture of light over the range of wave lengths included by the slits, cause errors[4] in the observed values of transmission. When, however, the homogeneous light is itself used to make the readings, the values obtained are free from both these

[4] These will tend to be most serious where the spectrophotometric curves show the greatest curvature, being determined mainly from the second derivatives of the luminosity curves resulting from (1) the energy distribution of the source, (2) the dispersion of the prism, (3) the visibility function, and (4) the spectral transmission or reflection of the sample. There are many kinds of work where the error may be negligible. Experimentally, such errors may be greatly reduced by the use of narrow slits. The slit widths which it is safe to use without making corrections to the results depend on the selectivity of the sample and the use of the results.

errors. Such values serve as valuable check points on those obtained with the continuous-spectrum source for the same wave-length settings, and in certain problems where the complete spectrophotometric curve is unnecessary they furnish sufficient data in themselves without further measurement.

The following wave lengths are commonly used for the above purposes: Hg 404.7, 435.8, 491.6, 546.1, and 578.0 (577.0+579.1) mμ; He 501.6, 587.6, and 667.8 mμ. When desirable, He 447.1 and 471.3 mμ are likewise used; and in certain cases Hg 623.4 mμ and He 706.5 mμ have been found practicable and have given results of value. Hg 546.1, Hg 578.0, He 501.6, and He 587.6 are used without stray-light filters, but appropriate filters are used at all the other wave lengths to eliminate stray light from the brighter lines. The particular filters used are noted below.

Another feature of great value in insuring the accuracy of data obtained on this apparatus and also in extending the range of reliable measurement to very low transmissions is the use of rotating sectors of known aperture. The position of the sector is shown in Fig. 1, just in front of the rhombs before the collimator slits of the spectrophotometer. Sectors having approximately 80, 70, 60, 50, 10, and 1 percent aperture were constructed. They may be used in pairs so that apertures of 40, 30, and 20 percent may be obtained, in addition to the others noted. These are rotated at high speed to eliminate flicker. They are used in two ways:

1. The rotating sector may be transferred from one beam to the other and its transmission measured in the usual manner for a transmission sample. This affords a check of the greatest importance on the accuracy of measurement. The sectors have been calibrated mechanically with an uncertainty of but ±0.00005. By measuring the transmission of the various sectors at various wave lengths the accuracy of the photometric scale of the instrument can be definitely checked. The accompanying table summarizes all the measurements of transmission made with the various sectors at the various wave lengths since the publication of RP 30. Previous comparisions of this kind may be found in two earlier publications.[5] Five different observers have taken part in the measurements shown in the table. The wave-length range covered is from 404.7 to 700 mμ. The general conclusion from these and the previous measurements is that the scale of the instrument is not in error

[5] RP 30, pp. 848–850. Priest, McNicholas, and Frehafer, *Some Tests of the Precision and Reliability of Measurements of Spectral Transmission by the Koenig-Martens Spectrophotometer*, J.O.S.A. and R.S.I., *8*, pp. 201–212; January, 1924.

TABLE 1. *Tests of accuracy of photometric scale of Koenig-Martens spectrophotometer by means of rotating sectors.*

Sector aperture, approx. value	Number of determinations	$\frac{T_S - T_M}{T_M} \times 100$*		
		Max.	Min.	Alg. mean
0.80	34	+1.2	−1.1	+0.03
.70	8	+0.5	−0.6	−0.18
.60	6	+0.4	−0.5	+0.02
.50	35	+0.7	−1.0	−0.14
.40	2	+0.2	−0.5	−0.16
.30	4	+0.1	−0.9	−0.20
.20	10	+0.4	−1.6	−0.53
.10	54	+1.6	−5.0	−0.94
.009	15	+2.9	−7.1	−3.35
**.20	3	+0.4	−0.5	−0.04
***.10	44	+1.6	−4.2	−0.66
**.10	12	+0.8	−1.1	−0.18

* T_M is the transmission of the sector as determined by mechanical calibration. T_S is the transmission of the sector as determined spectrophotometrically.

** Excluding values obtained at 530 mμ and shorter wave-lengths and at 650 mμ and longer wave-lengths.

*** Excluding values obtained at 404.7 and 700 mμ.

over the range of transmissions from 0.1 to 0.8 (and presumably to 1.0) but that results too low by 3 or 4 percent of the transmission may be obtained for transmissions of the order of magnitude of 0.01 (see next paragraph for method of elimination of this error). The accuracy of the results is directly affected, however, by the presence of stray light in the field. The stray light is to a considerable extent unpolarized and, if present in any important degree, results in values being obtained that are too low. This is well illustrated by the improved accuracy shown in the table for the 10 and 20 percent sectors when the measurements are restricted to the brighter regions of the spectrum. It may also be shown by values obtained before and after the instrument is cleaned.

2. It is apparent from the information given just above that reliable values of spectral transmission of the order of magnitude of one percent and lower would be difficult to obtain. However, the rotating sector may be used in such a way as to allow the sample to be measured relative to that of the sector. The sample and sector are geared to alternate in position, the sector being always in the blank beam. This brings the readings of the nicol, which might otherwise be in a region which the sectors have

themselves shown to be unreliable, into a part of the scale known to give accurate results. Transmissions between 1 and 10 percent are thus ordinarily measured relative to the 10 per cent sector, and transmissions 1 percent and below are measured relative to the 1 percent sector. In this way transmissions as low as 1/10 or 1/100 of one percent can be measured with considerable accuracy, the only loss of accuracy being due to the lowered precision resulting from the lowered brightness at which the measurements are made. The very high brightness of the incandescent-lamp and mercury-arc sources is of great value for such measurements.

Various tests have shown that the accuracy of measurement may be seriously reduced if the effects of stray light are not guarded against. This, of course, is true with most instruments and the remedy is the same in all cases: The optical surfaces should be kept as clean as possible and stray-light filters should be used where necessary, particularly in those regions where the sensitivity of the detector is relatively low. With the present apparatus the following filters have been found particularly suitable:

TABLE 2.

Source	Wave-length range	Filter
Incan. Hg* He	460 and below 404.7, 435.8 447.2	Jena 3654 (2.26 mm)
Incan. He	460–500 471.3	Corning G55A (5.60 mm)
Hg	491.6	Wratten 75
Incan. He	650 and above 667.8	Jena 4512 (2.28 mm)
Incan.	700 and above	Jena 4512 plus Corning G55A (2.28 mm) (5.60 mm)

* If the transmissions of the sample for 404.7 and 435.8 are widely different, it is best to use a violet filter such as Corning G586A with the 404.7 line.

Many materials show marked changes in transmission as the temperature of the sample is varied. The magnitude of such changes varies greatly from one sample or material to another and is a function of wave length for any particular sample. In extreme cases the change may

amount to as much as one percent of the transmission for one degree (Centigrade) change of temperature. Complete standardization or specification of the spectral transmission of a sample requires, therefore, that the temperature be noted at which the measurements are made.

This is done in practically all measurements of spectral transmission made with the above apparatus. In the case of liquids and glass samples of the proper size, the sample is mounted in a temperature control box. The temperature of the sample may in this way be controlled over the range from approximately 15° to 50°C. In case the sample cannot be mounted in the temperature control box, the temperature of the air close to the sample is noted at the time the measurements are made.

2. SPECTRAL REFLECTION MEASUREMENTS

With most of the samples submitted for reflection measurements the reflected light is partially diffused, and the precise specification of the type of illumination and the angle of observation is, in general, a matter of considerable importance. These experimental conditions are matters of choice dependent upon the purposes of the measurements. In the Bureau apparatus the sample is illuminated by light of essentially equal intensity from all directions; i.e., the illumination is, in effect, completely diffused, and the sample is viewed in a direction essentially at right angles to its surface. The quantity thus measured is known as the apparent normal reflectance for diffuse illumination. This type of illumination has the following advantages:

1. It is a type of illumination often approximated when samples are viewed near a window.

2. By the reciprocal relation[6] the quantity thus measured is equal to the reflectance for unidirectional normal illumination.

3. High illumination on the sample is readily obtainable.

4. The light reflected at right angles to the surface for this type of illumination is unpolarized, except for those materials exhibiting surface regularities, such as velvets, silks, etc.

Instead of attempting to measure the absolute reflectance, the reflectance, or brightness, is measured relative to that of magnesium oxide. This latter material is a reproducible, highly reflecting, highly diffusing material, and the experimental procedure is simplified and the certainty of the results is increased by making measurements relative to the oxide rather than by attempting to make them in absolute terms. In actual

[6] H. J. McNicholas, *Absolute Methods in Reflectometry*, Bur. Stand. Jour. Res., *1* (RP 3), pp. 29–73; July, 1928.

practice the oxide, which is somewhat fragile, is replaced by a white diffusing surface of porcelain. This was originally carefully measured relative to magnesium oxide and has been checked several times since. In making measurements, therefore, the sample is measured relative to the porcelain, and the results then computed relative to the oxide.

The method of securing the diffused illumination is shown in Fig. 1. The inside surface of the hemisphere is studded with 156 automobile headlight lamps and coated with magnesium oxide. The resulting brightness over the surface of the hemisphere is so nearly uniform that, as shown by tests, better approximation to perfect uniformity would not appreciably change the results obtained.

The sample and reference white standard occupy positions as shown near the center of the base of the hemisphere and the light reflected from them is brought into the spectrophotometer by way of the reflecting prism (4) and the lenses (1 and 2) as illustrated in Fig. 1. The sample and standard may be readily reversed in position by the observer, so that measurements are carried out exactly as for the transmission samples.

Two problems are encountered in making the reflection measurements that are ordinarily not present in transmission measurements:

1. It was noted above that certain samples such as velvets and silks possess surface structures which result in the light reflected normally being partially polarized even under diffuse illumination. This matter has been thoroughly considered in RP 30, and here as elsewhere this publication should be consulted for details. It is shown therein that the method of interchange of sample and standard greatly reduces the error that might otherwise be present in the measurements due to this effect. Furthermore, if the plane of polarization be determined, as can be done with a Martens photometer or on the Koenig-Martens spectrophotometer itself, the sample can be so cut that its plane of polarization is approximately at 45° to the planes of polarization of the instrument. By cutting the sample in this way and by reversing the sample and standard, polarization errors are made negligible. It should be noted that possible errors due to polarization of the reflected light are not limited to polarization instruments but are common to all spectrophotometers because of the polarizing action of the dispersing prism.

2. Because of the rather intense heat to which the sample is subjected, it is found in some cases to change color slightly during the measurements. This is prevented so far as possible by flowing air continuously through the hemisphere and by directing a stream of cool air

directly on the surface of the sample. In spite of this, slight changes are sometimes noticed. Readings are taken in such order, however, as to detect this change if present, and in most cases the values can be corrected to represent the sample before the change took place.

III. AUXILIARY METHODS

The visual method just described has certain outstanding features contributing to accuracy of measurement. These have been noted above, two of the most important being the self check on the photometric scale made possible by the rotating sectors and the maintenance of accuracy of measurement at low transmissions, also by means of the sectors. However, the visual method is inherently limited by the lack of sensibility in the end regions of the visible spectrum. This is rendered still more serious at the shorter wave lengths by the relative lack of energy emitted by the incandescent sources ordinarily used in spectrophotometric work. It is further emphasized by the increased dispersion in the blue and violet which also causes lowered sensibility unless the slits are kept adjusted to transmit a constant wave-length interval.

To supplement the visual method in these regions of lowered sensibility, the colorimetry section of the Bureau has for many years been using other methods—the photoelectric and photographic at the shorter wave lengths and the thermoelectric at the longer wave lengths. These will now be briefly described.

1. PHOTOELECTRIC METHOD

One of the first applications of the photoelectric cell to colorimetric research was made in connection with the color standardization program[7] of the Bureau of Standards. The photoelectric spectrophotometer first developed[8] was used for both spectral transmission and reflection measurements, a range from 380 to approximately 600 mμ being covered. Two potassium photoelectric cells were used in a sort of "Wheatstone-bridge" arrangement, a null method being employed and a Dolezalek quadrant electrometer serving as the indicator. For spectral transmission measurements, the amount of energy entering the spectrometer slit was varied by varying the distance of the source from the slit. The

[7] Initiated by Irwin G. Priest, Chief of the Colorimetry Section. See article by him, *The Work of the National Bureau of Standards on The Establishment of Color Standards and Methods of Color Specification*, Trans. I.E.S., *13*, pp. 38–49; Feb., 1918.

[8] K. S. Gibson, *Photoelectric Spectrophotometry by the Null Method*, Bur. Stand. Sci. Paper No. 349, October, 1919. In 1923 this method was superseded by an equal-deflections method, as described below.

photoelectric current thus produced was balanced by the photoelectric current of the second cell irradiated by a small lamp. The two lamps were operated in parallel, with suitable resistances, on a storage battery. The transmission sample was then inserted before the spectrometer slit and the balance restored by moving the lamp toward the slit the necessary amount. The transmission was then computed from the inverse squares of the distances. Rotating sectors were used to extend the range of measurement. (Measurements with the rotating sectors served also to intercheck the reliability of Talbot's law and that of the inverse-square law.)

For the diffuse reflection measurements the lamp was brought close to the spectrometer slit and left stationary; by means of a mirror and lens the energy was focused upon the sample at approximately 45°, and the energy leaving the sample at right angles to its surface entered the spectrometer slit. Either the test sample or the reference white surface ($MgCO_3$ or MgO) could be brought into the beam before the slit. The photoelectric current was balanced by that of the second cell, irradiated by the small lamp through an adjustable slit and milk glass diffusor. When the electrometer balance was destroyed by interchange of the sample and reference white, it could be restored by varying the width of the slit before the second cell; and the relative reflectance, for the particular angles of irradiation and reflection, was taken as the ratio of the slit widths. This method, while not as sound as the method used for the transmission measurements, proved fairly satisfactory.

The photoelectric null method described above was used to obtain published data for colored glasses,[9] dye solutions,[10] and colored papers,[11] and was in routine use for test measurements from 1918 to 1923.

In the latter year it was superseded by a simpler and more rapid method[12] designed only for spectral transmission measurements and used continually to the present time. This is an equal-deflections method with a galvanometer and a single cell. The apparatus is outlined in Fig. 2, which is taken from the paper to which reference has just been made. (The thermoelectric method for which the same diagram serves is described in the following section.)

The sample and a Brodhun sector are placed between two lenses used

[9] Bur. Stand. Sci. Papers No. 349; Bur. Stand. Tech. Papers No. 148.

[10] Bur. Stand. Sci. Papers No. 440.

[11] Bur. Stand. Tech. Papers No. 167.

[12] K. S. Gibson, *Direct-reading Photoelectric Measurement of Spectral Transmission*, J.O.S.A. and R.S.I., 7, pp. 693–704; 1923.

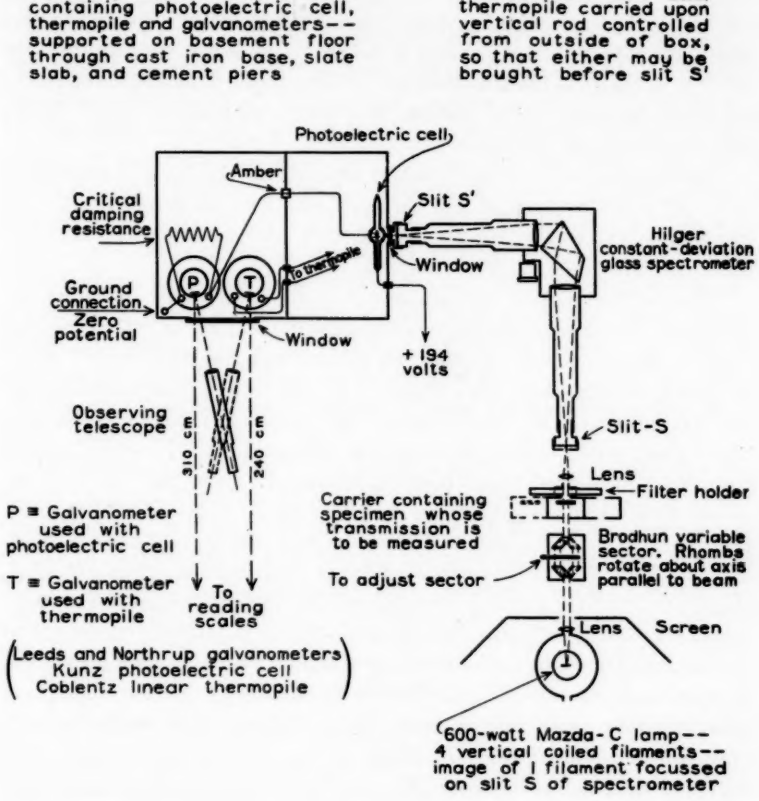

Two-compartment aluminum box containing photoelectric cell, thermopile and galvanometers--supported on basement floor through cast iron base, slate slab, and cement piers
Photoelectric cell and thermopile carried upon vertical rod controlled from outside of box, so that either may be brought before slit S'
Photoelectric cell
Amber
Critical damping resistance
Slit S'
Hilger constant-deviation glass spectrometer
To thermopile
Window
Ground connection Zero potential
Window
+ 194 volts
Observing telescope
310 cm
240 cm
Slit-S
Lens
Filter holder
Carrier containing specimen whose transmission is to be measured
Brodhun variable sector. Rhombs rotate about axis parallel to beam
To adjust sector
P ≡ Galvanometer used with photoelectric cell
T ≡ Galvanometer used with thermopile
To reading scales
Lens
Screen
(Leeds and Northrup galvanometers Kunz photoelectric cell Coblentz linear thermopile)
600-watt Mazda-C lamp--4 vertical coiled filaments--image of 1 filament focussed on slit S of spectrometer
ESSENTIAL PARTS OF APPARATUS FOR DIRECT-READING PHOTOELECTRIC (OR THERMOELECTRIC) MEASUREMENT OF SPECTRAL TRANSMISSION
Transmissions are read on the Brodhun variable sector
SCALE
0 10 20 30 40 50
cm
National Bureau of Standards
Div. IV-3 — K.S.G. — March, 1923

FIG. 2. *Outline of photoelectric and thermoelectric apparatus. This figure is taken from J.O.S.A. and R.S.I., 7, Fig. 3; 1923.*

to focus the image of a gas-filled lamp on the spectrometer slit. With the Brodhun sector set at 100.0 the galvanometer reading is noted; the sample is then removed from the beam and the sector adjusted to give the same galvanometer reading as before. This sector reading (divided by 100) is taken as the transmission of the sample. The lamp is operated on a storage battery and constancy of lamp current is assumed during the adjustment of the sector.

The working range of the method depends on the type of photoelectric cell. Both potassium and caesium cells have been used with this apparatus, the former for the violet, blue and green regions and the latter for the green, yellow, and red.

This method cannot be considered so fundamentally sound as the visual method described above. It is not self-checking as is that method via the rotating sectors. It may not give correct results if the cell is one in which the photoelectric current is not linearly proportional to the irradiation on the cell. Furthermore, the method of illumination is such that optical imperfections of the sample will more readily introduce error than in the described visual method. Whenever a new photoelectric cell is installed, the usual procedure is, therefore, to make careful spectrophotometric measurements with specimens of accurately known transmission. Unless satisfactory agreement is obtained the cell is not used. However, little trouble has been experienced in this respect. Throughout the life of the cell, also, values obtained by the photoelectric method are continually compared with those obtained visually, most important samples being measured by both methods. If in any particular case there is satisfactory agreement with the visual data obtained with the mercury source at 404.7, 435.8, and 491.6 mμ, or with the incandescent source in the neighborhood of 500 mμ, the photoelectric method is then considered to give reliable values throughout the blue and violet. Similar precautions to those required with the visual or any other method must, of course, be taken as regards stray energy, slit width, and wavelength calibration.

The method is fairly rapid and usually has had excellent reproducibility. Results thus obtained photoelectrically are illustrated in the publication describing the method and were used as noted in several other publications.[13] The method has also been used in routine test measurements for several years. Some results obtained by it are illus-

[13] J.O.S.A. and R.S.I., *9*, pp. 113–121; 1924. B.S. Sci. Paper No. 547, 1927. B.S. Misc. Pub. No. 114, 1931.

trated later in the present paper along with those obtained by other methods.

2. THERMOELECTRIC METHOD

To supplement the visual method in obtaining spectral transmission measurements in the red and to extend the measurements into the infrared, the thermoelectric method has been used for several years. The method is essentially the same as previously used by other investigators. The apparatus (Fig. 2) is the same as with the photoelectric method except that the thermopile and its galvanometer replace the photoelectric cell and its galvanometer and the Brodhun sector is removed. A ratio-of-deflections method is used. The galvanometer reading is noted when the sample is in the beam, when the sample is removed, and when the beam is cut off. The readings are repeated in such order as to eliminate error due to galvanometer drift, if present. Transmission is computed from the observed deflections when the sample is in and out of the beam.

The method has proved very reliable as judged by the agreement obtained with the visual method at those wave lengths in the red where the latter is still reliable. It is of special value in maintaining the accuracy of determination from 650 mμ towards the longer wave lengths. With the particular spectrometer used, the method can be employed out to approximately 2000 mμ, the maximum response occurring at 1150 mμ.

3. THE PHOTOGRAPHIC METHOD

The photographic method has been used to extend the measurements of spectral transmission from the blue and violet into the ultraviolet. The method used is known as the Hilger sector-photometer method. The method and apparatus have been described in previous publications.[14] Fig. 3 is taken from the first of the references noted and illustrates the essential optical and electrical features of the method. Radiant energy from the source may reach the slit by two alternative paths, as shown in the figure. An upper beam passes through a quartz lens and wedge, is refracted downwards through a rotating sector disk, which may be set at any desired aperture, and is deviated by the lower half of the quartz biprism to pass axially along the collimator of the spec-

[14] Gibson, Tyndall, McNicholas, Frehafer, Mathewson, *The Spectral Transmissive Properties of Dyes*, B.S. Sci. Paper No. 440, pp. 128–134; 1922. H. J. McNicholas, *Use of the Underwater Spark with the Hilger Sector Photometer in Ultraviolet Spectrophotometry*, B. S. Jour. Res., *1*, (RP 33) pp. 939–949; December, 1928.

trograph. A lower beam traverses a similar path through the lower wedge-lens and sector and is deviated by the upper half of the biprism to pass axially along the collimator like the first.

The spectrograph is thus fed by two beams from the same source. These are dispersed by the quartz prism, and a spectrum image of the slit is formed on the photographic plate. This spectrum is divided into two halves by a fine line extending along its entire length, which is the

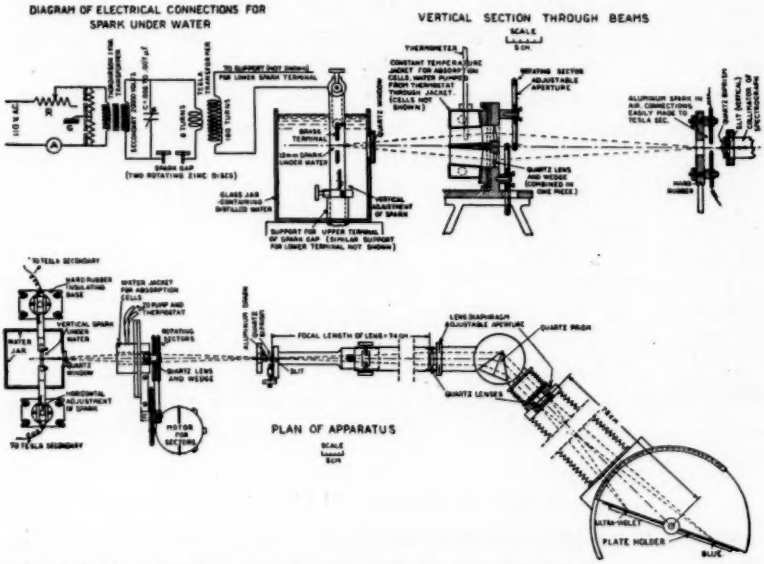


DIAGRAM OF ELECTRICAL CONNECTIONS FOR SPARK UNDER WATER
VERTICAL SECTION THROUGH BEAMS
PLAN OF APPARATUS
PLATE HOLDER

FIG. 3. *Diagram of Hilger sector photometer, quartz spectrograph, and accessory apparatus for ultraviolet spectrophotometry.*
This figure is taken from B. S. Sci. Paper No. 440, Fig. 3; 1922.

spectrum image of the refracting edge of the biprism. One half of this spectrum results from the upper beam, the other half from the lower beam.

If the ratio of the upper to the lower sector opening is unity and if the spark is in correct alignment, the densities of the two halves will be equal throughout their entire length, thus indicating equal intensities of the two beams. The plate may be raised or lowered in the plane of the spectrum, this permitting a series of spectrum photographs to be taken on each plate. Both sectors have a maximum opening of 180°, which may be adjusted to any desired value between 180° and zero. A

scale on each sector wheel gives the opening in percent of the maximum.

When measuring the transmittancy of a solution, a cell containing the solution is placed in one beam (e.g., the lower)[15] and a duplicate cell containing the solvent in the other. (The cells are inserted in openings in the constant temperature jacket, Fig. 3, upper half.) A series of exposures is made, each for a different ratio of upper to lower sector opening, the total exposure time (time of operation of the spark) being adjusted to give a normal blackening on the plate in each case.

Let E and E' represent the intensities of the lower and upper beams leaving the solution and solvent, respectively, S and S' the lower and upper sector openings, s and s' the corresponding effective exposure times through the rotating sectors.

The ratio E/E', which is the transmittancy of the solution, varies, in general, with the wave length of the radiant energy. For radiant energy of the particular wave length (or wave lengths) for which $E/E' = S'/S = s'/s$ there will result equal products of intensity and effective exposure time for each beam.

The assumption now made is that the equal quantities of energy thus delivered to the plate by each of the two beams produce equal blackenings on the plate at the wave length in question, or, in other words, that the transmittancy for any wave length at which equal blackenings are produced is given directly by the ratio of the sector openings.

The accuracy of this assumption has been questioned, but the work of Howe,[16] Gibson et al.,[17] Baly et al.,[18] and Hilger[19] has shown that the approximation is very good. In fact, so far as is known, it has never been demonstrated that the method gives results in error by more than the various experimental uncertainties.

Spectrophotometric data obtained at the Bureau by this method have been published[20] at various times and the method has been used in routine test measurements for about twelve years.

[15] On the Bureau apparatus both sectors are made adjustable and the usual procedure is to take the second half of the plate with the solution and solvent interchanged. In this position the same exposures are made as on the first half of the plate but in reverse order. Averaging the corresponding pairs of readings tends to eliminate errors resulting from imperfect match of the comparison spectra.

[16] Phys. Rev., *8*, pp. 674–688; 1916.

[17] B.S. Sci. Pap. No. 440, pp. 131–133; 1922.

[18] Roy. Soc. Proc., *113*, pp. 709–716; 1927.

[19] Advertising notices, 1928.

[20] B.S. Tech. Paper No. 148; 1920. B.S. Sci. Paper No. 440; 1922. Brode, J. Am. Chem. Soc., *46*, pp. 2032–2043; 1924; *48*, pp. 1877–1882, 1984–1988, 2193–2206; 1926. J. Phys. Chem., *30*, pp. 56–69; 1926. B.S. Res. Paper No. 47; 1929.

One feature of particular interest and importance in this method is the type of source used. The under-water high-tension discharge as used at the Bureau gives a continuous spectrum from above 500 mμ to below 220 mμ with no lines superposed. This makes for high precision in determining the point at which the two spectra are of equal density. The energy distribution in an under-water spark discharge has been published by Wyneken.[21]

IV. Comparison Of Spectral Transmission Data Obtained By The Various Methods.

Comparison of data obtained by the photographic method just described with that obtained by the other methods in the violet and blue has been adequately illustrated in the publications already noted, particularly in B. S. Sci. Paper No. 440. No further illustration of data obtained with the photographic method is made herein.

The illustrations given show, however, with one exception, comparisons of spectral transmission values obtained in the visible spectrum by the visual, photoelectric and thermoelectric methods. With the same exception these illustrations have *not* been prepared specially for this paper, but are shown exactly as they appear in publications or reports or in the files of the colorimetry section.

This exception is shown in Fig. 4. The purpose of this illustration is to show the very low values of transmission that are obtainable with the visual method by use of the rotating sector in the blank beam. The values in the green were measured relative to a sector that has a transmission of 0.00883. It may be seen that, although the transmissions in the green are but a few thousandths of one percent, the characteristic shape of the cobalt-blue transmission curve is readily brought out. The upper third of this illustration also shows one of the logarithmic forms used at the Bureau for the plotting of spectrophotometric data.

Figs. 5 and 6 show data obtained by visual, photoelectric, and thermoelectric methods for two of the four glasses loaned to American Photoelectric Corporation for test, upon which Mr. McMichael reports in the paper following this one. Attention is particularly called to:

1. The dates of the various determinations.

2. The degree of agreement between the visual and the photoelectric and thermoelectric methods, where the methods overlap, including the

[21] *Energieverteilung im kontinuierlichen spektrum des Aluminium-Unterwasserfunkens*, Ann. der Physik, *391*, pp. 1071–1088; 1928.

precise placing of the Hg 404.7 and 435.8 mμ (visual) values between the adjacent photoelectric values.

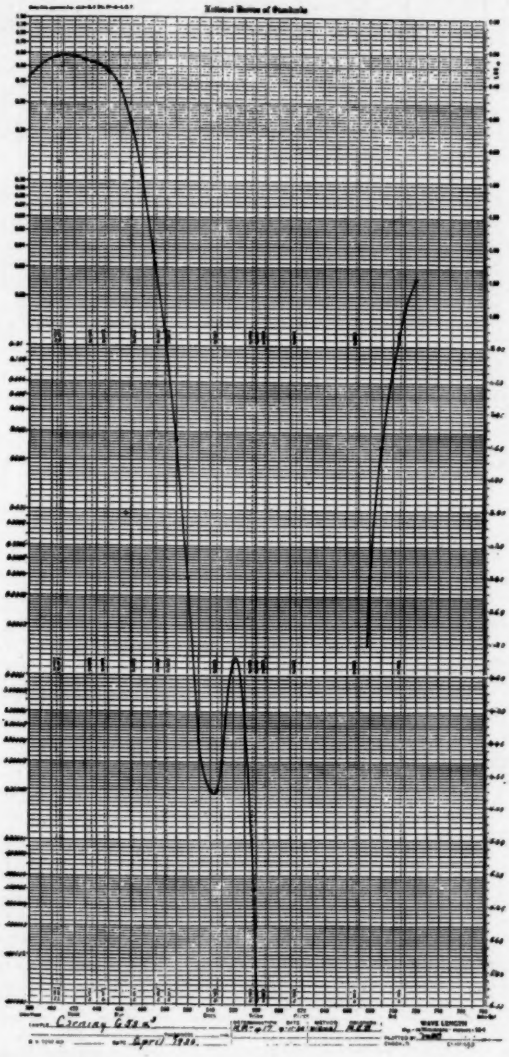


FIG. 4. *Showing extension of transmission measurements to very low values by means of Kœnig-Martens spectrophotometer and auxiliary sector disks.*

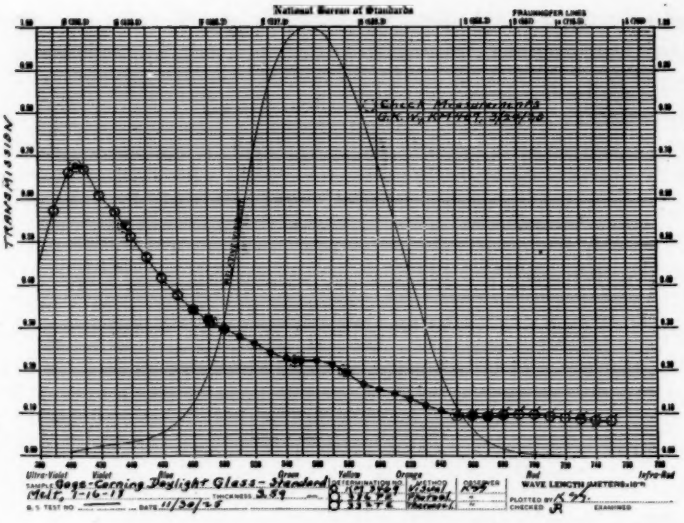


FIG. 5. *Illustrating degree of agreement obtained by visual, photoelectric, and thermoelectric methods in the measurement of a certain "daylite" glass.*

This glass and the one shown in Fig. 6 are referred to in the paper by McMichael and Barnard on this same program.

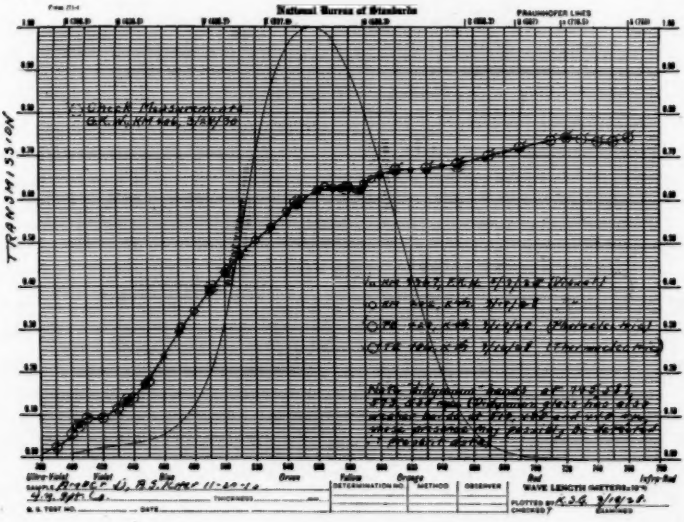


FIG. 6. *Illustrating degree of agreement obtained by visual, photoelectric, and thermoelectric methods in the measurement of a certain amber glass.*

This glass and the one shown in Fig. 5 are referred to in the paper by McMichael and Barnard on this same program.

3. The values obtained visually with the Hg and He light sources and plotted at the corresponding wave lengths.

4. The agreement between the recent check measurements and the previously determined data.

Similar data are shown in Fig. 7, which gives the transmission curve of a didymium glass submitted for test in 1929. These data are shown to illustrate the fine analysis necessary in the measurement of certain

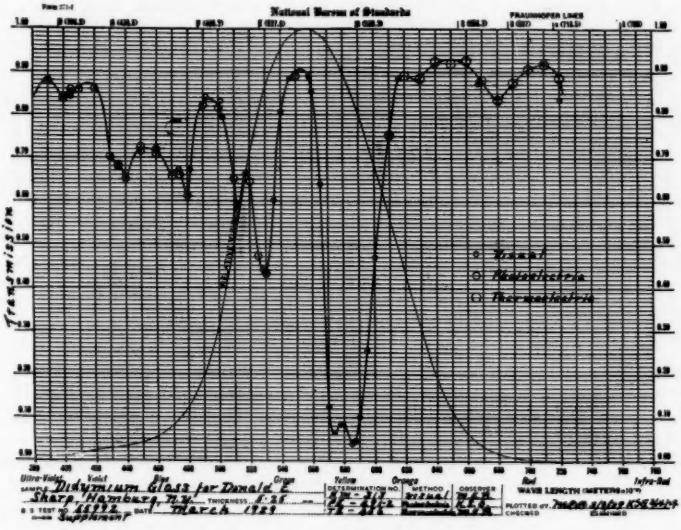


FIG. 7. *Transmission curve of didymium glass.*

Spectrophotometers should enable accurate measurements to be made of curves as "steep" as those shown, which are often found with red, orange, yellow, blue, and purple glasses.

glasses. The test was for purposes of information only. Further work would have been necessary, because of the discrepancies that may be noted in the data, if the glass had been intended as a spectrophotometric standard.

Fig. 8 is taken from the discussion of a paper by Crittenden and Taylor[22] showing comparative photometric and spectrophotometric tests on various colored glasses. In this case (fig. 8) may be noted:

[22] *An Interlaboratory Comparison of Colored Photometric Filters,* Trans. I.E.S., *24,* pp. 153–197; Feb., 1929. The above graph is given on page 198 of the discussion following the paper.

1. The degree of agreement between the respective methods.

2. The use of the 10 percent sector for the lower values of transmission and the degree of agreement between such values and those obtained without the sector.

3. The weighting of values obtained by the various methods in adopting values of transmission for the glass.

4. The effect of stray light on the values obtained visually with the incandescent source from 680 to 720 mμ, even though a red filter was used over the ocular. The discrepancy here is somewhat larger than usu-

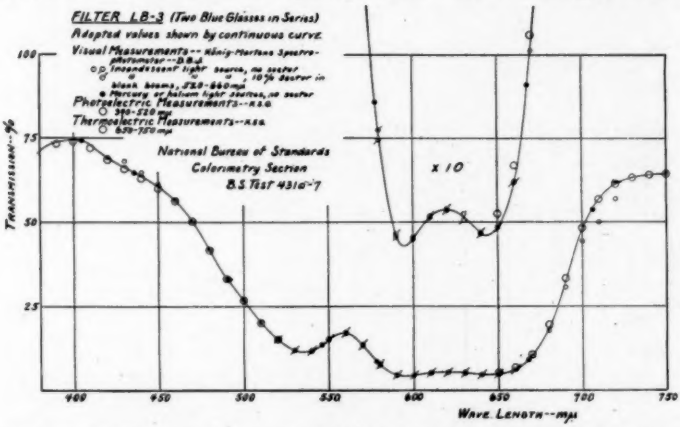


FIG. 8. *Illustrating degree of agreement obtained by visual, photoelectric, and thermoelectric methods in the measurement of a cobalt blue glass filter.*

This filter is one of several used by Crittenden and Taylor in an inter-laboratory comparison of colored photometric filters. The figure is taken from Trans. I.E.S., 24, p. 198; 1929.

ally obtained. It may be greatly reduced by using for a stray-light filter a combination of red and cobalt blue glass instead of a red glass alone.

5. The effect of stray energy on the thermoelectric values from 650 to 670 mμ.

The spectral transmission of a blue glass known as R4–28 is shown in Fig. 9. This illustration is taken from a report by the author dated December 19, 1929. This particular glass is one of four measured in the national standardizing laboratories of England, France, Germany and the United States in connection with an international comparison of photometric filters.

In addition to the points to which attention has already been called in connection with the previous illustrations, the following may be noted:

1. The degree of precision of the visual data is indicated by the radius of curvature of the plotted circles. The mean of the average deviations from the mean at the various wave lengths from 450 to 670 mμ (not

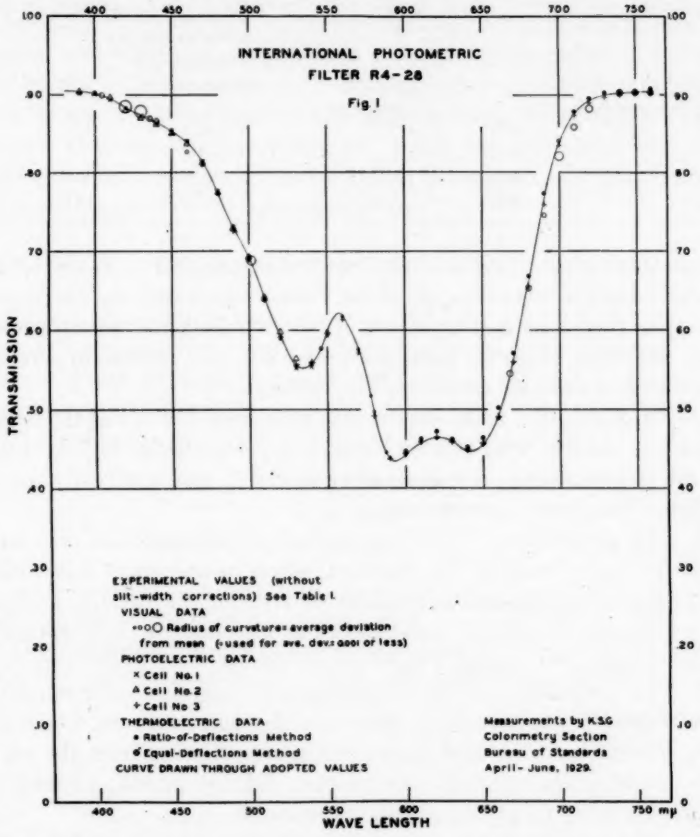


FIG. 9. *Illustrating degree of agreement obtained by various spectrophotometric methods as noted. This cobalt blue glass is one of four measured in the national standardizing laboratories of England, France, Germany, and the United States. The figure is taken from an unpublished report by the author.*

including the Hg and He values) is 0.0011 or between 0.1 and 0.2 percent of the transmission.

2. Tests were made by means of the rotating sectors during the measurements. The 80, 70, 60, and 50 percent sectors were chosen for this

purpose, the respective wave lengths being chosen at which the transmission of the sector approximately duplicated that of the glass. The following average values were obtained:

Sector	Percentage deviation from mechanically measured value
80%	+0.1
70%	− .2
60%	+ .1
50%	− .2

From these measurements it was concluded that there was no certain error in the photometric scale of the visual instrument, and the uncertainty in the visual measurements of transmission from 500 to 650 mμ was considered to be not greater than ±0.001, or a maximum percentage uncertainty of not exceeding ±0.2 percent.

3. Three different photoelectric cells were used. No. 1 was the potassium cell which had been in use for several years previously. No. 2 was an old potassium cell, not as sensitive as No. 1, and apparently not as reliable. No. 3 was a caesium cell.

4. The agreement of the three methods of measurement was such that the uncertainty in the adopted values of spectral transmission (allowing for the known uncertainty or error of the various methods in certain regions of low sensitivity) was estimated as not exceeding ±0.002 below 500 mμ and ±0.005 above 650 mμ.

5. The computation of the transmission of light at a color temperature of 2080°K was part of the purpose of the measurements. The probable error in the computed light transmission, derived from the probable errors in the spectral transmission, did not exceed ±0.0002 or approximately 0.04 percent of the transmission.

SUMMARY

Brief descriptions have been given above of the methods and apparatus used in making spectrophotometric measurements in the colorimetry section of the Bureau of Standards. Full descriptions have been given in the publications to which reference is made. What is noted particularly in the present paper are those features of the methods which tend to insure reliability in the values obtained. It is shown that the photometric scale of the Koenig-Martens spectrophotometer can be in-

dependently checked and greatly extended by means of the rotating sectors. The means taken to eliminate wave-length, slit-width, and stray-light errors are noted, particularly the use of homogeneous light of certain wave lengths in the measurement of transmission.

The degree of agreement ordinarily obtained with the visual, photoelectric, and thermoelectric methods is shown by several illustrations. The reliability of the non-visual methods is checked by their agreement with the visual method at those wave lengths where the latter is reliable. In turn, the non-visual methods serve to maintain the reliability of the measurements throughout the end regions of the visible spectrum where the sensibility of the eye is extremely low.

American Institute of Physics. As announced by Dr. Karl T. Compton, Chairman of the Governing Board (Science **73,** No. 1902, 636, June 12, 1931) the organization of the American Institute of Physics is now in progress.

The Executive Council has approved the appointment of

F. K. RICHTMYER
P. D. FOOTE
L. A. JONES

as representatives of the Optical Society of America on the Governing Board of the Institute.

These representatives will serve until December 31, 1931, by which time it is expected a permanent organization will be completed.

(Signed) L. B. TUCKERMAN
Secretary

SOME COMPARATIVE SPECTROPHOTOMETRIC MEASUREMENTS

By Monroe Barnard and Paul McMichael*

[American Photoelectric Corporation, New York, N.Y.

Received March 21, 1931]

This paper is presented on invitation from the Committee on Meetings and Programs, Optical Society of America, who asked us to give such definite evidence as is practicable regarding the actual results obtained with the spectrophotometric instrument which we have developed, and now made commercially available.

The A.P.C. photoelectric spectrophotometer is an instrument developed by American Photoelectric Corporation for determining the spectral absorption characteristics of materials in industry whose colors are matters of significance.

Any A.P.C. photoelectric spectrophotometer is an assembly of at least six different pieces of apparatus, any of which is interchangeable with any other similar unit, to wit:

(1) constant deviation spectrometer, with light source
(2) slidewire bridge
(3) galvanometer
(4) A.P.C. photoelectric unit, which contains the
(5) photoelectric tube
(6) batteries for illuminating source, filament supply and amplifying circuit.

An instrument comprising these six unit pieces of apparatus is employed for determining the spectral absorption characteristics of transparent materials. For translucent or opaque substances an additional piece of apparatus is added, namely, the A.P.C. opaque illuminator.

This instrument has been designed so as to have incorporated in it the following desirable features:

(1) simplicity of operation and maintenance
(2) interchangeability of parts
(3) adaptability to miscellaneous colorimetry laboratory requirements, such as determination of the relative brightness of materials at different angles of observation
(4) adaptability to precision measurements of either liquids or solids.

* Presented at special session of the Optical Society of America on Spectrophotometry and the Use of Photoelectric Methods in Colorimetry, New York, February 26, 1931.

In the precise measurement of the spectral transmission or reflection characteristics of a substance there are several possible sources of error, some of which are common to any spectrophotometric method, and some which are particular to photoelectric spectrophotometry. These may be grouped as follows:

POSSIBLE SOURCES OF ERROR IN ANY SPECTROPHOTOMETRIC METHOD

(1) Variations in the spectral composition of the color of the material during its analysis, which may be caused by heat from the illuminating source

(2) Inaccurate wave-length calibration of spectrometer

(3) Incorrect illumination of the material under examination

(4) Significant stray light in spectrometer.

POSSIBLE SOURCES OF ERROR IN PHOTOELECTRIC SPECTROPHOTOMETRY

(1) Departure from linearity of amplification

(2) Lack of linearity of photoelectric tube response

(3) Variations of selectivity of different photoelectric tubes

(4) Variations in voltage of power supply to amplifying circuit

(5) Variations in the characteristics of the amplifying circuits during measurements

(6) Variation in linearity of the recording instrument

(7) Time lag of recording mechanical parts with its consequent distortion of measurements

(8) Multiplicity of movable contacts with its consequent greater possibility of instability in the electrical circuits

(9) Non-interchangeability of illuminating sources and electronic tubes

(10) Variations in the color and intensity of the source of illumination.

The A.P.C. photoelectric spectrophotometer is a commercial instrument for which all these possible sources of error have been carefully evaluated and they are either wholly eliminated or provided against.

TRANSMISSION MEASUREMENT

For spectral transmission measurements the light source affixed to the spectrometer is a tungsten filament lamp connected with a 6-volt storage battery.

The collimating and ocular slits of the spectrometer are so adjusted

as to pass a spectral band of any desired width. Usually, however, for commerical use, the spectrometer is equipped at its ocular end with a fixed slit of such width as to pass a spectral band of from 7 to 12 millimicrons width at 587.6 millimicrons, the familiar helium line.

The operation of the instrument in determining the transmission factor of a transparent substance at any desired wave length is as follows:

(1) The spectrometer is set at the desired wave length

(2) The slide on the side of the photoelectric unit is set at Position 1 so that none of the energy transmitted through the spectrometer is incident to the photoelectric tube

(3) With toggle switch on panel of the photoelectric unit set at zero, the circuit is balanced by manipulating the dials controlling the resistances therein, the galvanometer being used as a zero indicator. This establishes the zero of the scale on which the reading is made

(4) The slide, which carries the sample, is now set at Position 2 so that all of the energy transmitted through the spectrometer is incident to the photoelectric tube

(5) With toggle switch set at 100, the circuit is again balanced by turning the dials on its resistances, the galvanometer serving as zero indicator as before. This establishes the 100 of the scale on which the reading is made

(6) The slide is now set at Position 3 so that the sample is interposed between the spectrometer and the photoelectric tube

(7) With toggle switch set at READ, the circuit is again balanced, but this time the slide wire bridge is used for the purpose, the galvanometer serving as zero indicator. The proportion of the total incident light transmitted by the sample is read directly in percent on the scale of the slidewire bridge.

The length of time required to establish the scale and to make an individual reading varies from 15 to 20 seconds, depending upon the manipulative skill of the operator.

As many individual readings are made at any particular wave length as may be required to bring the probable error within the desired limit. Usually, in commercial practise, at least three readings are made for each setting of the spectrometer.

Values are determined at as many different wave lengths as may be necessary in order to define the spectral absorption characteristics with the required degree of precision. Of course, with a substance that has

widely varying spectral absorption characteristics, values must be determined at more wave lengths than with a material whose characteristics do not vary widely within relatively narrow spectral zones. Usually, in commercial practise, fifteen values at 20 millimicron intervals are sufficient to define the spectral absorption characteristics with sufficient precision, and in daily routine control work two or three at different wave lengths have often proven adequate.

REFLECTION MEASUREMENT

In measuring the spectral absorption characteristics of translucent or opaque substances with this instrument, the manipulation is substantially the same as for transparent materials, except that an A.P.C. opaque illuminator is added to the six pieces of apparatus used for transmission measurements. This accessory is set up at the collimating end of the spectrometer. Essentially, it is a hollow hemisphere, internally coated with white sphere paint as a diffusive reflecting surface, and provided with four equally-spaced tungsten filament lamps as the illuminating source, these being connected in series with five 6-volt storage batteries.

This opaque illuminator is provided with a 2-position slide that carries the sample, and also a block of pure magnesium carbonate, or any other desired comparative standard. The circuit is balanced to establish zero with no energy being transmitted, again balanced to establish 100 with all the energy reflected by the magnesium carbonate block in the spectral band for which the spectrometer is set, and the reading is made on the scale of the slidewire bridge directly in percent of the energy reflected by the magnesium carbonate block, or by the alternative comparative standard employed.

ACCURACY OF PHOTOELECTRIC UNIT

The degree of accuracy of measurement obtainable with this instrument is limited by the accuracy of the spectrometer, rather than by the accuracy of the photoelectric unit. This is demonstrated by Tables 1 and 2 on which are shown four analyses made of a filter belonging to U. S. Bureau of Standards and described as A. O. Co. Amber B, B. S. Letter 11-20-16.

All of the measurements in the first and second columns of Table 1 were made with a Bausch and Lomb No. 2700 constant deviation type spectrometer. This instrument was equipped with special diaphragms in order to decrease the amount of stray light. At the ocular end it was

provided with a fixed slit of such width as to pass a spectral band 7.4 millimicrons wide at 587.6 millimicrons.

Similarly, all of the measurements in the third and fourth columns were made with a Gaertner L 230 wave-length spectrometer. At its ocular end this instrument was equipped with a fixed slit of such width as to pass a spectral band 10.1 millimicrons wide at 587.6 millimicrons.

The collimating slits of both spectrometers were never wider than 0.2 millimeter, except for measurements in the spectral region below 460 millimicrons.

The photoelectric unit and the photoelectric tubes used for making the measurements set down in Column 1 were entirely different from those used for making the measurements in Column 2, and, in like manner, the photoelectric unit and the photoelectric tubes used for making the measurements in Column 3 were entirely different from those employed in securing the data given in Column 4.

TABLE 1. *U. S. Bureau of Standards Filter A. O. Co. Amber B, B. S. Letter 11-20-16*

	Transmission factors—Percent					
Spectrometer	Bausch & Lomb			Gaertner		
Photoelectric unit	1	2		1	2	
Photoelectric tubes	2 & 3	1 & 4		2 & 3	1 & 4	
Wave length millimicrons			Difference			Difference
420	11.9	11.7	0.2	11.1	11.0	0.1
440	14.8	14.9	0.1	15.6	15.4	0.2
460	24.3	24.1	0.2	24.8	24.5	0.3
480	34.6	34.5	0.1	35.1	35.1	0.0
500	42.6	42.6	0.0	43.9	43.5	0.4
520	50.6	50.5	0.1	51.1	50.9	0.2
540	56.8	56.8	0.0	57.6	57.7	0.1
560	62.0	61.9	0.1	62.5	62.4	0.1
580	62.8	62.8	0.0	62.7	62.9	0.2
600	65.5	65.3	0.2	66.1	66.1	0.0
620	67.2	67.2	0.0	67.4	67.4	0.0
640	67.6	67.6	0.0	68.1	68.1	0.0
660	69.1	69.0	0.1	69.6	69.6	0.0
680	71.3	71.2	0.1	72.1	72.0	0.1
700	72.7	72.7	0.0	73.4	73.5	0.1
Average difference			0.08			0.12

It will be noted that, despite the fact that entirely different photoelectric units and different photoelectric tubes were used for securing the

data in Columns 1 and 2, and again in Columns 3 and 4, nevertheless the average differences were only 0.08% and 0.12% respectively.

On Table 2 the readings secured with the same photoelectric units and the same photoelectric tubes, but with different makes of spectrometers, are set down in juxtaposition, so as to show the relatively greater differences in the readings when different spectrometers were used.

TABLE 2. *U. S. Bureau of Standards Filter A. O. Co. Amber B, B. S. Letter 11-20-16.*

	Transmission factors—Percent					
Photoelectric unit	1			2		
Photoelectric tubes	2 & 3			1 & 4		
Spectrometer	Bausch & Lomb	Gaertner		Bausch & Lomb	Gaertner	
Wave length millimicrons			Difference			Difference
420	11.9	11.1	0.8	11.7	11.0	0.7
440	14.8	15.6	0.8	14.9	15.4	0.5
460	24.3	24.8	0.5	24.1	24.5	0.4
480	34.6	35.1	0.5	34.5	35.1	0.6
500	42.6	43.9	1.3	42.6	43.5	0.9
520	50.6	51.1	0.5	50.5	50.9	0.4
540	56.8	57.6	0.8	56.8	57.7	0.9
560	62.0	62.5	0.5	61.9	62.4	0.5
580	62.8	62.7	0.1	62.8	62.9	0.1
600	65.5	66.1	0.6	65.3	66.1	0.8
620	67.2	67.4	0.2	67.2	67.4	0.2
640	67.6	68.1	0.5	67.6	68.1	0.5
660	69.1	69.6	0.5	69.0	69.6	0.6
680	71.3	72.1	0.8	71.2	72.0	0.8
700	72.7	73.4	0.7	72.7	73.5	0.8
Average difference			0.61			0.58

It will be noted that, although the same photoelectric unit and the same photoelectric tubes were used for securing the data in Columns 1 and 2, and likewise in Columns 3 and 4, nevertheless the average differences were 0.61% and 0.58% respectively, or more than four times the maximum average difference on Table 1.

Thus it would appear that any A.P.C. photoelectric unit enables one to measure transmission factors to about 0.1% of the total energy incident to the sample, and that variations in the values secured with this instrument of 0.5% or more may result with different spectrometers, even when they have been carefully calibrated.

In order to ascertain the accuracy of this instrument, we analysed four filters belonging to U. S. Bureau of Standards, which were loaned to us through the courtesy of Mr. Irwin G. Priest, Chief of the Colorimetry Section.

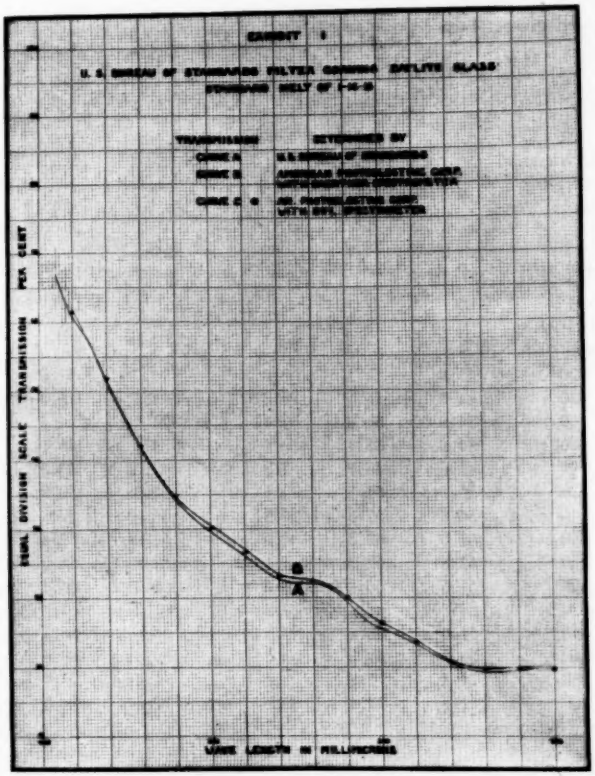


FIG. 1. *U. S. Bureau of Standards Filter Corning Daylite Glass. Standard Melt of 1–16–18*

Spectral transmission	*determined by*
Curve A	*U. S. Bureau of Standards*
Curve B	*American Photoelectric Corp., with Gaertner Spectrometer*
Curve C	*American Photoelectric Corp., with B & L Spectrometer*

The analyses were made just as in commercial practise, readings being taken at 20 millimicron intervals from 420 to 700 on three filters and from 460 to 800 millimicrons on the fourth filter. We had no information whatsoever as to the values adopted by U. S. Bureau of Standards until

after we had submitted our data to Mr. Priest, who then afforded us opportunity to make comparison. The adopted values of U. S. Bureau of Standards are based upon determinations made at 10 millimicron intervals by Dr. K. S. Gibson and Miss Geraldine K. Walker of the Colorimetry Section. The comparisons are shown graphically on Exhibits 1 to 4 and arithmetically on Tables 3 to 6 herewith.

COMPARATIVE MEASUREMENTS

All the curves marked *B* on these exhibits were graphed from those A. P.C. values which showed the greatest average differences from the adopted values of U. S. Bureau of Standards. In other words, these B curves were derived from A.P.C. readings whose average differences were from 0.04% to 0.79% greater than the average differences of those A.P.C. readings which more nearly coincided with Bureau values.

On Fig. 1, Curve *A*, derived from the values adopted by U. S. Bureau of Standards, shows the spectral transmission characteristics of a blue filter described as Corning Daylite Glass Standard Melt of 1–

TABLE 3. *U. S. Bureau of Standards Filter Corning Daylite Glass Standard Melt of 1–16–18*

A—U. S. Bureau of Standards—adopted values
B—A.P.C. values with B & L spectrometer
C—A.P.C. values with Gaertner spectrometer

	Transmission			Differences			Differences		
	Percent of incident energy			Percent of incident energy			Percent of transmitted energy		
Wave length millimicrons	A	B	C	D A-B	E A-C	F B-C	D/A	E/A	F/B
420	60.8	61.5	61.8	0.7	1.0	0.3	1.2	1.6	0.5
440	51.2	51.9	51.7	0.7	0.5	0.2	1.4	1.0	0.4
460	41.6	42.0	41.9	0.4	0.3	0.1	1.0	0.7	0.2
480	34.2	34.9	34.6	0.7	0.4	0.3	2.0	1.2	0.9
500	29.6	30.1	30.7	0.5	1.1	0.6	1.7	3.7	2.0
520	26.2	26.6	27.1	0.4	0.9	0.5	1.5	3.4	1.9
540	22.7	23.1	23.3	0.4	0.6	0.2	1.8	2.6	0.9
560	22.2	22.4	22.6	0.2	0.4	0.2	0.9	1.8	0.9
580	19.3	20.1	20.0	0.8	0.7	0.1	4.1	3.6	0.5
600	15.5	16.4	16.3	0.9	0.8	0.1	5.8	5.2	0.6
620	13.3	13.7	13.9	0.4	0.6	0.2	3.0	4.5	1.5
640	10.6	10.8	11.0	0.2	0.4	0.2	1.9	3.8	1.9
660	9.3	9.8	9.8	0.5	0.5	0.0	5.4	5.4	0.0
680	9.6	9.8	10.1	0.2	0.5	0.3	2.1	5.2	3.1
700	9.7	9.8	10.2	0.1	0.5	0.4	1.0	5.2	4.1
Av. diff.—% of incident energy				0.47	0.61	0.25			
Average difference—% of transmitted energy							2.32	3.26	1.29

16–18. Curve *B* was graphed from A.P.C. values determined with a Gaertner spectrometer, and Curve *C*, indicated by the circled dots, from A.P.C. values found with a B & L spectrometer. It will be noted that, while the contours of all three curves are similar, the transmission values of *B* and *C* are uniformly slightly higher than those of *A*.

These differences are shown on Table 3. It is interesting to note that the average difference between the adopted values of U. S. Bureau of Standards and those obtained with a Bausch and Lomb spectrometer by American Photoelectric Corporation is slightly less than the average differences shown on Table 2, where different spectrometers were used with all other units identical, but, on the other hand, more than four times greater than the average differences shown on Table 1, where the same spectrometers were used with all other units different.

Perhaps, the relatively insignificant differences amongst the three sets of values in Columns *A*, *B* and *C* are more clearly set forth by translation into terms of color vision, as on Table 3-A.

TABLE 3-A

A—U.S. Bureau of Standards—adopted values
B—A.P.C. values with B & L spectrometer
C—A.P.C. values with Gaertner spectrometer
Values in terms of primary color sensations

	A	B	C
Violet—%	50.0	49.7	49.5
Green—%	27.6	27.8	27.9
Red—%	22.4	22.5	22.6

Values in terms of color vision

	A	B	C
Dominant wave length—mμ	476	477	477
Brightness—%	21.5	22.0	22.1
Purity—%	15.5	16.0	15.5

On Fig. 2, Curve *A*, derived from the values adopted by U. S. Bureau of Standards, shows the spectral transmission characteristics of a filter described as Amber *B*, B.S. Letter 11–20–16, while Curve *B* was graphed from the values found by American Photoelectric Corporation with a Gaertner spectrometer. While the contours of the two curves are similar, the values found by American Photoelectric Corporation are generally slightly higher than the adopted values of U. S. Bureau of Standards. It is interesting to note that these curves intersect at 568 millimicrons and again at 583 millimicrons, both within the zone of high eye sensitivity. It should be remembered, when comparing these

curves, that Curve *A* was derived from measurements at 10 millimicron intervals, whereas Curve *B* was graphed from observations made at 20 millimicron intervals as in ordinary commercial practise.

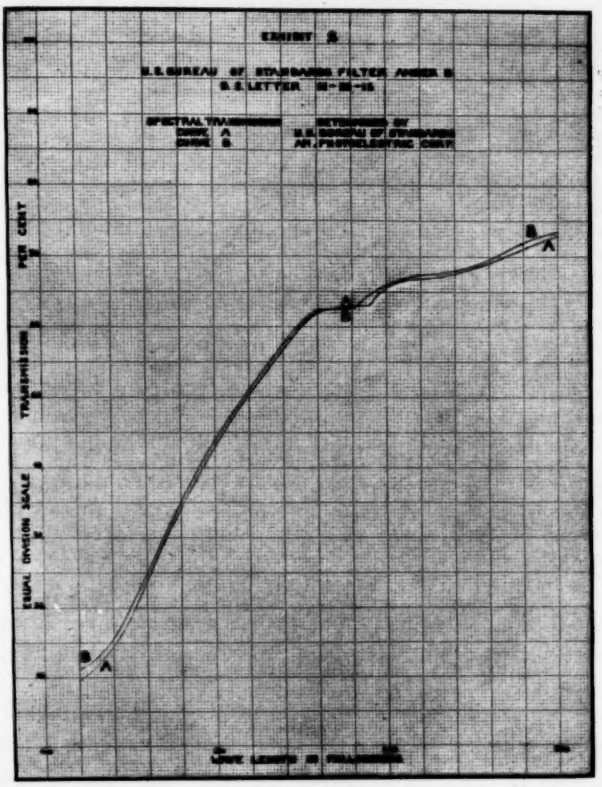


FIG. 2. *U. S. Bureau of Standards Filter Amber B, B. S. Letter 11–20–16*

Spectral transmission	*determined by*
Curve A	*U. S. Bureau of Standards*
Curve B	*American Photoelectric Corporation*

The differences between the curves on Fig. 2, and also the differences between the adopted values of U. S. Bureau of Standards and those obtained by American Photoelectric Corporation with a Bausch and Lomb spectrometer, all are shown on Table 4.

On Fig. 3, Curve *A*, derived from the adopted values of Dr. Gibson and Miss Walker, shows the spectral transmission characteristics of a

TABLE 4 *U. S. Bureau of Standards Filter Amber B, B. S. Letter 11-20-16*
A—U. S. Bureau of Standards—adopted values
B—A.P.C. values with B & L spectrometer
C—A.P.C. values with Gaertner spectrometer

	Transmission			Differences			Differences		
	Percent of incident energy			Percent of incident energy			Percent of transmitted energy		
Wave length millimicrons	A	B	C	D A-B	E A-C	F B-C	D/A	E/A	F/B
420	9.5	11.9	11.1	2.4	1.6	0.8	25.3	16.8	6.7
440	14.3	14.8	15.6	0.5	1.3	0.8	3.5	9.1	5.4
460	23.8	24.3	24.8	0.5	1.0	0.5	2.1	4.2	2.1
480	34.2	34.6	35.1	0.4	0.9	0.5	1.2	2.6	1.4
500	43.0	42.6	43.9	0.4	0.9	1.3	0.9	2.1	3.1
520	50.4	50.6	51.1	0.2	0.7	0.5	0.4	1.4	1.0
540	56.9	56.8	57.6	0.1	0.7	0.8	0.2	1.2	1.4
560	62.1	62.0	62.5	0.1	0.4	0.5	0.2	0.6	0.8
580	63.0	62.8	62.7	0.2	0.3	0.1	0.3	0.5	0.2
600	65.6	65.5	66.1	0.1	0.5	0.6	0.2	0.8	0.9
620	66.8	67.2	67.4	0.4	0.6	0.2	0.6	0.9	0.3
640	67.6	67.6	68.1	0.0	0.5	0.5	0.0	0.7	0.7
660	69.2	69.1	69.6	0.1	0.4	0.5	0.1	0.6	0.7
680	71.1	71.3	72.1	0.2	1.0	0.8	0.3	1.4	1.1
700	72.9	72.7	73.4	0.2	0.5	0.7	0.3	0.7	1.0
Av. diff.—% of incident energy				0.39	0.75	0.61			
Average difference—% of transmitted energy							2.37	2.91	1.79

filter described as Jena 5560 Alpha Prime, whereas Curve *B* was made from values determined by American Photoelectric Corporation with a Gaertner spectrometer.

The differences betwen the curves on Fig. 3, and also the differences between the adopted values of U. S. Bureau of Standards and those found by American Photoelectric Corporation with a Bausch and Lomb spectrometer, all are shown on Table 5.

On Fig. 4, Curve *A*, from the adopted values of U. S. Bureau of Standards, shows the spectral transmission characteristics of a filter described as A.O. Co. 7 Alpha, while Curve *B* was graphed from the values found by American Photoelectric Corporation with a Gaertner spectrometer. Attention is directed particularly to the fact that the scale upon which these values were plotted is twice as long as that employed on the preceding exhibits. This enlargement of the scale was made because the values were so small, particularly in the visible spectrum betwenn 460 and 650 millimicrons, that the difference could not

otherwise be shown graphically. It will be noted that the transmission factors of this filter were determined by American Photoelectric Corporation to 800 millimicrons. These measurements could have been extended further into the infrared, the only limiting factor being the gradually diminishing response of the photoelectric tube to the energy of longer wave lengths.

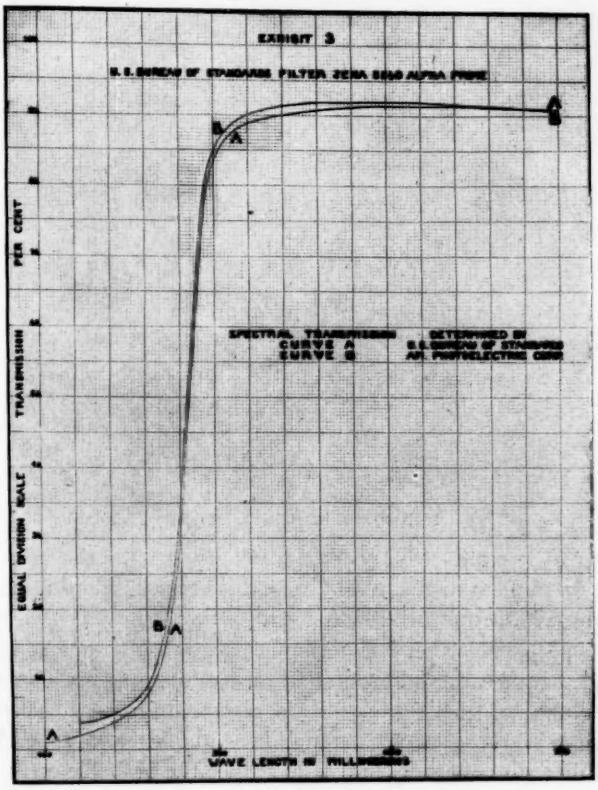


FIG. 3. *U. S. Bureau of Standards Filter Jena 5560 alpha prime.*

The differences between the curves on Fig. 4, and also the differences between the adopted values of U. S. Bureau of Standards and those found by American Photoelectric Corporation with a Bausch and Lomb spectrometer, all are shown on Table 6.

TABLE 5. *U. S. Bureau of Standards Filter Jena 5560 Alpha Prime*
A—U. S. Bureau of Standards—adopted values
B—A.P.C. values with B & L spectrometer
C—A.P.C. values with Gaertner spectrometer

	Transmission			Differences			Differences		
	Percent of incident energy			Percent of incident energy			Percent of transmitted energy		
Wave length millimicrons	A	B	C	D A-B	E A-C	F B-C	D/A	E/A	F/B
420	2.0	2.9	3.8	0.9	1.8	0.9	45.0	90.0	31.0
440	3.9	4.5	4.8	0.6	0.9	0.3	15.4	23.1	6.7
460	8.0	8.7	9.2	0.7	1.2	0.5	8.8	15.0	5.7
480	31.0	31.0	35.5	0.0	4.5	4.5	0.0	14.5	14.5
490	65.0	65.3	69.2	0.3	4.2	3.9	0.5	6.5	6.0
500	83.5	84.5	85.0	1.0	1.5	0.5	1.2	1.8	0.6
520	88.8	89.5	90.1	0.7	1.3	0.6	0.8	1.5	0.7
540	90.0	90.7	91.3	0.7	1.3	0.6	0.8	1.4	0.7
560	90.7	91.5	91.9	0.8	1.2	0.4	0.9	1.3	0.4
580	91.2	91.8	91.9	0.6	0.7	0.1	0.7	0.8	0.1
600	91.4	92.0	92.1	0.6	0.7	0.1	0.7	0.8	0.1
620	91.4	91.6	92.0	0.2	0.6	0.4	0.2	0.7	0.4
640	91.4	91.2	91.7	0.2	0.3	0.5	0.2	0.3	0.5
660	91.2	90.8	91.4	0.4	0.2	0.6	0.4	0.2	0.7
680	91.0	90.8	91.0	0.2	0.0	0.2	0.2	0.0	0.2
700	90.8	90.8	90.7	0.0	0.1	0.1	0.0	0.1	0.1
Av. diff.—% of incident energy				0.49	1.28	0.89			
Average difference—% of transmitted energy							1.61	9.88	4.28

ACCURACY OF INSTRUMENT

In order to determine whether or not any difference in the value found with this instrument might result from a difference in the position of the sample relative to the spectrometer, two series of readings were made with the spectrometer setting unchanged throughout, one series with the sample between the light source and the collimating end of the spectrometer, and the other series with the sample interposed between the fixed ocular slit of the spectrometer and the photoelectric tube. A sufficient number of readings was made to reduce the probable error to less than 0.05% for each series. The difference between the averages for the two series was 0.04%.

Three different individuals were engaged in making the A.P.C. measurements upon which are based the data reported, any one of the three, indiscriminately, performing one or another of the two tasks involved, namely, (1) balancing the electrical circuits, and (2) reading the slide-wire bridge. Of course, in commercial practise, one person performs both

tasks, about 15 to 20 seconds being required for an individual reading, but for this interlaboratory check it was considered best to divide the work as stated in order to demonstrate that observers might be interchanged as well as the unit pieces of apparatus without resultant error.

It was our conclusion, based upon careful observation and repeated checking, that any operator might make an error of plus or minus 0.1%

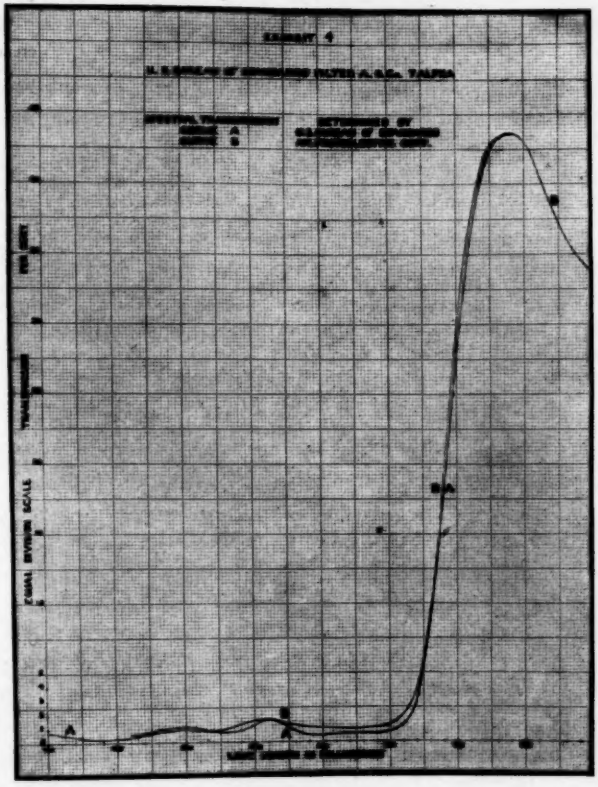


FIG. 4. *U. S. Bureau of Standards Filter A. O. Co. 7 alpha.*

in balancing the electrical circuits, and that any operator might make a similar error in reading the scale on the slidewire bridge, so that the aggregate error on any one particular reading might be as much as plus or minus 0.2%. For all the A.P.C. values given herein, a sufficient number of readings was made, at least five in every instance, to reduce the probable error to less than 0.1%.

With this instrument all measurements of transmission or reflection values are made on an equal division scale divided into 200 parts. However, values on this scale may be estimated to one part in one thousand, or 0.1%. It is obvious, therefore, that the proportionate error in a value measured on such a scale increases as the reading assumes a lower numerical value. Thus, for transmission or reflection values of 70% or more, the proportionate error in the measured value is less than 0.2%. On the other hand, for a measured value of 10%, the proportionate error is about 1.0%, and so on progressively for still lower values, until with a measured value of but 1.0% the proportionate error is about 10.0%.

TABLE 6. *U. S. Bureau of Standards Filter A. O. Co. 7 Alpha*
A—U. S. Bureau of Standards—adopted values
B—A.P.C. values with B & L spectrometer
C—A.P.C. values with Gaertner spectrometer

	Transmission			Differences			Differences		
	Percent of incident energy			Percent of incident energy			Percent of transmitted energy		
Wave length millimicrons	A	B	C	D A-B	E A-C	F B-C	D/A	E/A	F/B
460	0.35	0.7	0.6	0.35	0.25	0.1	100.0	71.4	14.3
470	0.55	0.9	0.7	0.35	0.15	0.2	63.6	27.1	22.2
480	0.74	1.0	0.9	0.26	0.16	0.1	35.1	21.6	10.0
500	0.90	1.1	0.9	0.20	0.00	0.2	22.2	0.0	18.2
520	0.76	1.0	0.8	0.24	0.04	0.2	31.6	4.0	20.0
540	0.82	1.4	1.3	0.58	0.48	0.1	70.7	58.5	7.1
560	1.58	1.9	1.7	0.32	0.12	0.2	20.3	7.6	10.5
580	0.80	1.3	1.2	0.50	0.40	0.1	62.5	50.0	7.7
600	0.48	1.1	1.0	0.62	0.52	0.1	129.2	108.3	9.1
620	0.60	1.1	0.9	0.50	0.30	0.2	83.3	50.0	18.2
640	0.61	1.4	1.1	0.79	0.49	0.3	129.5	80.3	21.4
660	1.25	2.1	2.0	0.85	0.75	0.1	68.0	60.0	4.8
680	8.70	8.5	9.4	0.20	0.70	0.9	2.3	8.0	10.6
700	28.20	28.4	30.0	0.20	1.80	1.6	0.7	6.4	5.6
720	41.10	40.9	41.8	0.20	0.70	0.9	0.5	1.7	2.2
740	43.60	43.8	43.7	0.20	0.10	0.1	0.5	0.2	0.2
Av. diff.—% of incident energy				0.40	0.44	0.34			
Average difference—% of transmitted energy							51.3	34.7	11.4

Regular stock types of unit apparatus were used throughout in determining the A.P.C. values. A greater degree of accuracy of measurement could have been secured by using a more finely graduated slide-wire bridge and by narrowing the fixed ocular slits with which both spectrometers were equipped. However, if a greater degree of accuracy of measurement had been so obtained, the rapidity with which individ-

ual readings could have been made would have been decreased. Such refinements can not be justified in an instrument designed for commercial use. If greater accuracy of measurement is demanded, relatively greater progress in this direction will probably be attained by effort looking toward the elimination of stray light in the spectrometer, as this is considered to be the largest probable source of error.

Since this interlaboratory check was made, we have been afforded opportunity to use a spectrometer especially designed according to suggestions of A.P.C. engineers so as to decrease stray light. With this spectrometer, a sufficient number of comparative measurements has already been made to enable us to say that all the *A.P.C.* values herein are, in general, slightly higher than would have been obtained with this new spectrometer. With such better-designed spectrometers commercially available, data of even greater accuracy than those reported can be secured in everyday commercial practise, because it would appear that the degree of accuracy of measurement is limited by the degree of accuracy of the spectrometer employed, rather than by the degree of accuracy of the photoelectric unit.

SPEED AND ADAPTABILITY

The approximate average length of time required for the individual readings upon which the A.P.C. values are based was about twenty (20) seconds, and the total elapsed time for determining the factors at 15 or 16 different wave lengths was about 45 or 50 minutes, i.e. for each of the complete analyses as shown on the exhibits.

If the photoelectric tube employed in this instrument has its relative maximum response in the zone between 500 and 600 milimicrons, then the degree of accuracy of measurement in the outlying zones of the visible spectrum may be increased by employing filters in the manner proposed by John W. T. Walsh.* If measurements in the ultraviolet or infrared are to be made with this instrument, it is to be understood that photoelectric tubes are used whose relative maximum responses are in the regions wherein the measurements are to be made. In order to determine the spectral absorption characteristics of any material outside the visible spectrum, all that is required with this instrument is a photoelectric tube responsive to the energy of the wave lengths to be measured and a spectrometer that will segregate this energy into the required substantially monochromatic bands.

* Photometry, 1926, page 277 et seq.

Mention has been made that this instrument was so designed as to lend itself readily to miscellaneous colorimetry laboratory requirements, such as the determination of the relative brightness of materials at different angles of observation. In this connection, mention is made that American Photoelectric Corporation has developed an accessory for use with the photoelectric unit incorporated in its photoelectric spectrophotometer, the A.P.C. angle reflector, which enables one to measure with precision the relative proportion of the light reflected from a surface at any desired angle which is reflected at any other angle. Thus, one may measure the relative amounts of specular and diffuse reflection from each side of a material, as for example, the opposite sides of a sample of paper, or the relative amounts of specular and diffuse reflection from the surfaces of two different samples placed back to back, as, for example, two painted metal strips.

Values may be secured with this instrument directly in percent of any desired reference scale. For example, if the spectral absorption characteristics are wanted in terms of eye sensitivity, this result is attained by the simple expedient of establishing the 100 of the scale on which the measurement is to be made by setting the dial on the slide-wire bridge to the value of the relative eye response at the wave length where the measurement is to be made. Thus, automatically, the mathematical computations necessary for conversion are eliminated.

Apart from the speed with which color analyses can be made with this instrument, its most valuable feature is that transmission values are obtained directly in percent of the total energy incident to the sample, and reflection values in similar terms of any desired standard reflecting surface. Spectrophotometric curves are interesting as exhibits, but, if any real use is to be made of data set forth in this manner values must first be picked off the curve. It is only from such mathematical expressions that one can determine the reflection factor, the dominant wave length, brightness and purity of the color of a material.

Is it not preferable to secure the precision data essential for the definition of a color directly, rather than by the slow, tedious and fallible process of picking values off a spectrophotometric curve developed by a mechanical process having inherent possible sources of error? We of the American Photoelectric Corporation believe so.

DISCUSSION OF PAPER BY McMICHAEL AND BARNARD "SOME COMPARATIVE SPECTROPHOTOMETRIC MEASUREMENTS"

MR. IRWIN G. PRIEST: Mr. President, I am very gratified at the presentation of this paper, and for this reason: I believe that (in spite of the fact that great publicity has been given to photoelectric methods in recent years) this is the first time that anyone has ever given anything like an approximation to an adequate comparison of data which would lead one to have any degree of confidence in photoelectric measurements throughout the visible spectrum, or which would enable one to estimate in any way to what extent he might depend upon the measurements.

I am glad for the sake of public information that Mr. McMichael has seen fit to do this. I think we must admit that the accuracy is not entirely adequate to precision color specifications, as I shall show in a few moments. On the other hand, I do not wish to overemphasize this point because I think, for a first attempt in development work, the degree of agreement between the photoelectric measurements by the American Photoelectric Corporation and our own at the Bureau of Standards is rather encouraging. It is rather difficult to discuss the degree of agreement from the point of view of color specification. However, we may attempt it.

Suppose you wish to use the data in this way: You wish to define the color of a sample, of which the spectral transmission is given, so that if another sample measured on another instrument (assuming that instrument correct), is found to have the same spectral transmission, or a transmission approximating that or different from it, you can decide whether or not the color is matched closely enough to suit you. To illustrate such use of the data, I have had computed from Mr. McMichael's data and our own, differences which can be expressed in terms of colorimetric quantities. Taking their spectral transmission data and ours, we have computed the sunlight transmission of each of the samples separately for the two sets of data. For the four samples we have these discrepancies. (The speaker referred to table herewith.) For that low-transmission sample (A. O. Co. 7α), of course, our judgment is that the photoelectric measurements fall down very badly. Mr. McMichael himself pointed out the proportionate error. The relative error becomes very large for low transmission because their absolute error is

a constant. So we have for the filter of lowest transmission a difference of 39 percent of the transmission. But as soon as we get to the high values, we have much more creditable performance. For another glass the difference may be 2.6 percent, for another 1 percent, and for that amber glass only 0.4 of 1 percent. We have also computed the trilinear coordinates for each set of data, for each sample, and the corresponding dominant wave lengths and purities. I shall not bother to read the dominant-wave-length and purity data because that might not mean much. But we have tried to indicate the differences in chromaticity, or what perhaps is more commonly called the quality of color. If you assume their data in one case and ours in another, we find, in the case of one of these samples, that the color difference is of a degree of magnitude comparable with two Jones hue-steps. (I don't know how many of you know what a Jones hue-step is, but perhaps some of you do. I will tell you in a moment.) For another sample it is 0.2 of a Jones hue-step, for another 0.3, and for the other 0.26.

For those who do not know the magnitude of a Jones hue-step, I should say that it is about ten times what I would call the least difference that is commonly taken account of in commercial colorimetry. To be very specific, one industry that has the most to do with precision color grading is the vegetable oil industry. Thousands of dollars pass hands on the question of whether a color of an oil is this or is that, when the difference in color between this or that oil is well nigh imperceptible. For the filter of lowest transmission (A.O. Co. 7α), the discrepancy would be about 20 times this vanishingly small difference. For the other filters, however, the differences between our determinations and the American Photoelectric Corporation would be in each case about two or three of these minute vanishing differences on which money changes hands. I hope that I have succeeded in that comparison—without going into figures and wave lengths, purities and so forth—in giving you an idea in a gross way, of the degree of difference expressed in some manner in terms of dollars and cents in trade.

I have just one more remark to make, Mr. President, and that is I do not believe Mr. McMichael is justified in attributing his errors to the spectrometers. It seems to me that if the error is in the spectrometer at all, it must be in the manner of using it. I expect Dr. Gibson will comment more fully on that. In the meantime, I wish to extend to Mr. McMichael my thanks for the progress that has been made and wish him well for success in eliminating the discrepancies that I have indicated. Perhaps he will desire to ask me to eliminate our errors. I would like to suggest

Table to accompany Mr. Priest's discussion of Mr. McMichael's paper.

Comparison of data given by (1) Bur. of Stands., (2) Am. Photoelec. Corp.
Comparison in terms of colorimetric characteristics
(All on basis of Abbot-Priest Sunlight and O.S.A. Excitations)

Filter	Authority	Transmission for sunlight	Trilinear coordinates			Dom. wave length	Purity	Chromaticity diff.* (by Judd)
			r	*g*	*b*			
	(1)	.00943	.41401	.39618	.18981	575.3	.5314	
A. O. Co.	(2)	.01308	.41315	.37305	.21380	580.4	.4499	
7α	(1)–(2)	−.00365	+.00086	+.02313	−.02399	−5.1	+.0815	2.1
	Rel. dif.	−38.7%						
Corning	(1)	.22008	.21204	.26263	.52534	474.8	.1581	
Daylite	(2)	.22593	.21459	.26389	.52152	474.6+	.1529	
glass	(1)–(2)	−.00585	−.00255	−.00126	+.00382	+0.2	+.0052	0.2_3
melt	Rel. dif.	−2.65%						
1–16–18								
	(1)	.86715	.47113	.44919	.07968	574.2	.8334	
Jena	(2)	.87597	.46805	.44783	.08412	574.1+	.8229	
5560α′	(1)–(2)	−.00882	+.00308	+.00136	−.00444	+0.1	+.0105	0.2_8
	Rel. dif.	−1.07%						
A. O. Co.	(1)	.57485	.44457	.40243	.15299	578.1−	.6375	
Amber B	(2)	.57727	.44168	.40029	.15803	578.1	.6230	
B. S. letter	(1)–(2)	−.00242	+.00289	+.00214	−.00504	0.0	+.0145	0.2_6
11–20–16	Rel. dif.	−.42%						

* Units, equivalent to Jones hue-step.

that my colleague, Dr. Judd, has brought up two pieces of glass which will serve to illustrate the magnitude of the color differences we have been discussing.

DR. DEANE B. JUDD: Perhaps you can see one of the spots looks greenish and one looks reddish. I took the trilinear coordinates, which were derived from the Bureau of Standards' measurements of that low transmission sample, which is a sample that will strain the abilities of any spectrophotometer. From those, the trilinear coordinates which we believe to be very close to the correct ones, since they result from the Bureau of Standards' measurements, I picked out the corresponding combination of Lovibond glasses; that is, the combination which gave the same trilinear coordinates. Then I took the trilinear coordinates developed from the measurements of the American Photoelectric Corporation and chose another combination of Lovibond glasses which cor-

responded to those trilinear coordinates. The difference that you see here is an example of the chromaticity difference between the two specifications which are supposed to refer to the same piece of glass. (The Lovibond combinations exhibited were as follows: (1) For the B.S. specifications: 3.4 yellow, 0.5 red. (2) For the A.P.C. specification: 2.6 yellow, 1.7 red.)

MR. PRIEST: This is the worst case, the case in which the two determinations differed most widely. When you look at those two colors, you see a color difference corresponding to the difference between two samples one of which has been constructed to satisfy our specifications while the other has been constructed to satisfy the A. P. C. specifications. Bear in mind that is the worst case. And if we may speak rather grossly for the other three cases, the difference in color would be of the order of magnitude of about one-tenth of that difference.

In regard to the comparison of these values, there is one item of information I would like to give to justify our believing that we are right where these differences occur. Any open-minded man would be willing to admit, I suppose, that we might be wrong and the American Photoelectric Corporation might be right on these discrepancies, but, fortunately for us, we could make a direct check, at least on the sign of the differences, and that was done. It happened that two of these glasses had such chromaticities that they were comparatively near together, but somewhat apart. So that by putting them in a field of a Martens photometer and equating the brightness, we immediately had a qualitative check on the difference in wave length. We had computed the dominant wave lengths on both sets of data and the hue difference as immediately perceptible in the field was in accord with our own data, that is, the difference between those two glasses qualitatively checked with our spectral transmissions rather than with the American Photoelectric.

MR. MCMICHAEL: I want to disclaim one thing. Mr. Priest has seen fit to credit me with the development of this instrument. I wish very emphatically to disclaim that. This instrument was developed by Messrs. Monroe Barnard and Harold D. Ellsworth, and the credit is theirs.

DR. K. S. GIBSON: It should be quite apparent to all of you that this paper and these measurements are of interest to the Colorimetry Section. I agree with Mr. Priest in saying that we feel highly pleased with the results obtained in these measurements. We think the American Photoelectric Corporation is to be congratulated when we compare

these with some other comparative measurements which have been made in the past by different people, with different apparatus.

The main thesis of Mr. McMichael's paper was stated to be something like this, that the accuracy of measurement obtainable with the A. P. C. spectrophotometer was limited by the accuracy of the spectrometer rather than by the accuracy of the A. P. C. photoelectric outfit.

There are two things involved there. In the first place, I think he should have used the word "precision" or "reproducibility," rather than "accuracy." I don't think "accuracy" is primarily involved in the comparison of one or the other instrument. Accuracy, we hope, is involved when it comes to comparing results with ours, but when it is a question of comparing results obtained with his apparatus with different photoelectric cells and different spectrometers, it is largely a question of reproducibility or precision.

I am afraid some members of the audience may get the impression that the spectrometers are bearing the brunt of the lack of precision pointed out by Mr. McMichael, whereas I think he has left out one very important item, and that is the precision of the operator, because a spectrometer will do in general only what the operator makes it do. I don't believe Mr. McMichael has demonstrated that these two spectrometers would not give identical results if they had both been calibrated perfectly so far as wave length is concerned and if they had both been used with the same identical slit widths, which they were not.

Furthermore, of course, the precision obtainable with the A. P. C. outfit, as pointed out by Mr. McMichael and mentioned by Mr. Priest, is seriously limited at the low transmissions. That I consider at present to be the most serious trouble with the apparatus. When you get down to transmissions of the order of magnitude of 1 percent or one-half percent, then apparently there may be errors which may be as large as 50 or 100 percent of the transmission. That is why these differences get serious for those values.

Mr. McMichael chose the worst possible case for illustration on the graphs; that is, he picked out those values which showed the largest deviation from our values. If he had picked out the average of all the data which he obtained, he would have secured more favorable agreement, so that the comparison was really more favorable than was indicated by the graphs.

In our analysis of his data, we found that, on the average, all through the spectrum for each one of the four samples, there was a slight positive deviation of his values from ours, and this was so consistent, averaging

about .004 or .005, regardless of the sample, that we can't help feeling there may be some little instrumental error in the A. P. C. apparatus which we can hope will be eliminated and bring the results into still further agreement.

MR. E. C. CRITTENDEN: Mr. President, there are two points I would like to bring out in the discussion at this place. One is that we are perhaps apt to expect too much of these instruments on the basis of assuming an accuracy in the case of visual spectrophotometry which is not actually obtained. A paper published by Mr. A. H. Taylor and myself a couple of years ago in the Transactions of the Illuminating Engineering Society gives some data bearing upon that point. Measurements reported in that paper were made to get a comparison among laboratories on the photometric measurements of colored filters. One of the methods of measurement used was spectrophotometric observation, in which several of the laboratories used visual methods.

I may say that in general the agreement reported here between the American Photoelectric Corporation and the Bureau is very much better than the agreement we obtained between most of the laboratories which took part in that measurement. There were very few among the seven laboratories then reporting that agreed as well as these two do in this case. The agreement on the low transmissions in that case was very much worse than in this case and on the high transmissions it was certainly no better than is reported here.

The other point I would like to make is in behalf of our Committee on Meetings and Programs. Since this discussion seems to involve some criticism of the precision or accuracy of these instruments, I wish to express our appreciation of the gentlemen who have agreed to come in here and present their results for such discussion and criticism. Every instrument which we knew was being put on the market for these purposes was given an opportunity for representation; these authors and the gentlemen who are to present the next paper, therefore, are the ones who are bold enough to present their data for public criticism.

DR. SELIG HECHT: I am very little concerned with the accuracy or the precision of the measurements that have been presented, but I feel that it is proper to make a general criticism of the procedure adopted by the makers of this instrument.

It is the usual practice—and I believe it should continue to be the normal practice—in any scientific society whenever an instrument is presented, that the theory of that instrument be presented clearly, openly. Nobody wants to buy or work with a pig in a poke. The descrip-

tion of this instrument has deliberately not been made available publicly up to the present time; it thus seems a little beside the point to discuss the reproducibility and the accuracy of its performance without our knowing what the instrument is.

MR. MCMICHAEL: Dr. Hecht failed to mention that the operation of this instrument was demonstrated to him, that he was given a copy of the drawing of the electrical circuits that accompanied our application for letters patent, and that Messrs. Barnard and Ellsworth, in a long discussion with him, explained everything about this instrument there is to know except details of the amplifying circuits. We will make even these details public just as soon as we secure action on the case now pending before the U. S. Patent Office.

CHAIRMAN JONES: I have been informed that Mr. Barnard would like to make a statement relative to one of the spectrometers used in the test of the A. P. C. instrument.

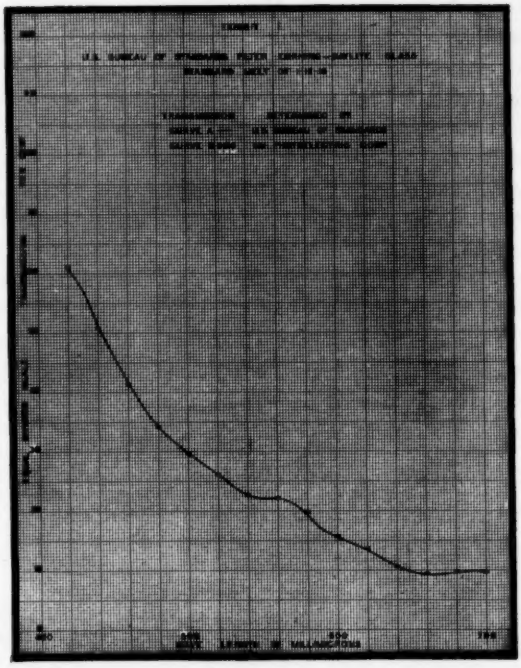
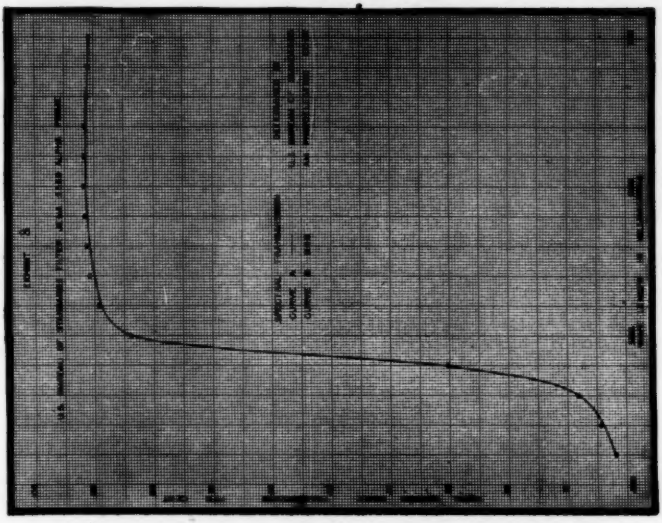
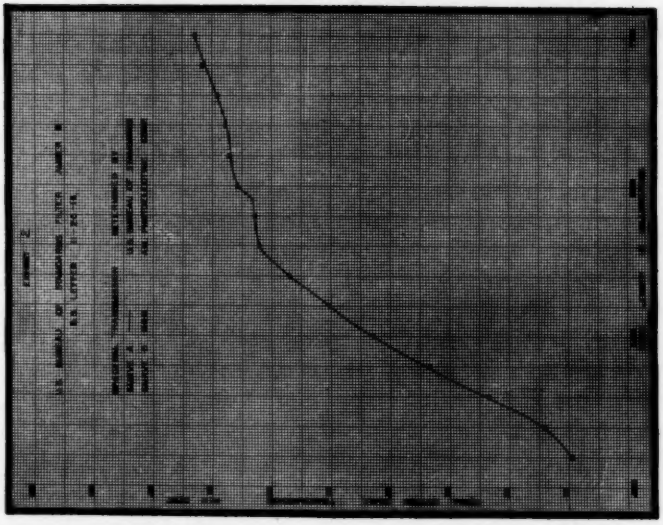
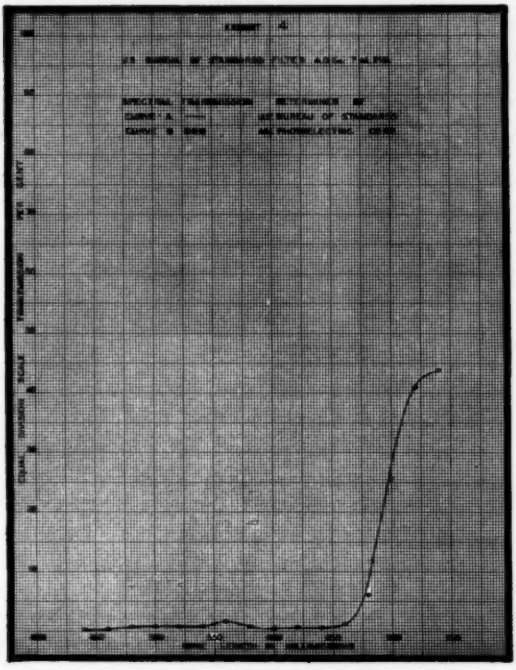
MR. BARNARD: The only thing was this: I thought perhaps there might be some impression created that one or the other spectrometer was being condemned. That was not the purpose and in fairness to the comparison of the spectrometers we did not want to create that impression. In the case of one which did have considerable stray light due, of course, largely to mechanical defects, that is being corrected by the manufacturer.

COMMUNICATED DISCUSSION FROM MR. MCMICHAEL

Dr. Gibson has been kind enough to direct attention to the fact that the comparative graphs were derived from those A. P. C. measurements that differed most widely from the values adopted by U. S. Bureau of Standards. He has expressed doubt, however, as to our having demonstrated our thesis, which is that the accuracy of measurements made with these instruments is limited by the accuracy of the spectrometers employed, rather than by the accuracy of the A. P. C. units.

In our paper, we mentioned the fact that since the completion of the interlaboratory check, the results of which are given therein, we have been afforded opportunity to make further measurements with a spectrometer designed in accordance with suggestions of A. P. C. engineers so that stray light is substantially eliminated.

Since the paper was presented we have obtained the same filters again from the Bureau of Standards and have made measurements with the new spectrometer. These more recent measurements, compared with the adopted values of U. S. Bureau of Standards, are shown graphically

in the figures designated as Exhibits 1 to 4 inclusive. We consider that these closer checks sustain our contention, and we believe that the degree of accuracy of measurements made with these instruments is limited by the accuracy of the spectrometers used, rather than by the accuracy of the A. P. C. photoelectric units.

(The exhibits just mentioned follow.)